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CONTENTS OF VOLUME 11, 1936.

No. 1. JANUARY.

Ryoichi MATSUDA: The Electrolytic Formation of Persulphate. Part I 1

Tetsuya ISHIKAWA and Toshitomo BABA: A Viscosity Formula for Binary Mixtures, the Association Degrees of Constituents being taken into Consideration. XII 8

Mioji UENAKA and Bennosuke KUBOTA: On the Formation of Symmetrical Dibenzo-cyclo-docosane-dione 19

Yoshiyuki TOYAMA and Tomotaro TSUCHIYA: Decenoic Acid $C_{10}H_{18}O_2$ in Sperm Head Oil 26

Yoshiyuki TOYAMA and Goroku AKIYAMA: The Highly Unsaturated Alcohols in Sperm Blubber Oil 29

Munenari TANAKA: Gewinnung der festen Fiber aus Reisstroh . . 35

Noriyoshi MORITA und Toshizo TITANI: Über den Unterschied in der Isotopenzusammensetzung von Luft- und Wassersauerstoff. (Vorläufige Mitteilung.) 36

Ryutaro TSUCHIDA, Masahisa KOBAYASHI, and Akira NAKAMURA: The Configuration of Chlorobisdimethylglyoximoammine-cobalt . . 38

No. 2. FEBRUARY.

Buhei SAKURAI: Electrolytic Reduction of *N*-Methylsuccinimide and *N*-Ethylsuccinimide 41

Shigeaki YAMASAKI: Über die Dampfphasehydrolyse 43

Yuichi NAKATSUKA: Di-8-oxychinolin-innerkomplexsalz des zweiwertigen Silbers 45

Yuichi NAKATSUKA und Hirosi IINUMA: Über Didimethylglyoxim-diammin-kobalt (III)-salze und ihre Konfiguration 48

Masao HARADA und Toshizo TITANI: Die Geschwindigkeit der Austauschreaktion der Wasserstoffatome zwischen Zucker und Wasser. (Vorläufige Mitteilung.) 55

Osamu KIMURA: On the Viscosity of the Critical Mixture of Ternary System Benzene-Alcohol-Water 57

Tetsuya ISHIKAWA and Toshitomo BABA: A Viscosity Formula for Binary Mixtures, the Association Degrees of Constituents being taken into Consideration. Summary 64

No. 3. MARCH.

The papers published in this number are dedicated to Dr. Rikō Majima by his pupils in celebration of his sixtieth birthday.

Professor Rikō MAJIMA (with a Portrait) 103

Riichiro YAMASAKI and **Kentaro ICHIHARA**: On the Composition of Rape Seed Oil 114

Rin-nosuko SHIBATA und **Minoru OKUYAMA**: Über die Produkte der Einwirkung von Monochloressigsäure auf Naphthole 117

Kashichi ONO and **Minoru IMOTO**: Synthesis of Vanillin from Cresols. I. Synthesis of Homopyrocatechin 127

Kashichi ONO and **Taichiro OYAMADA**: On the Reaction between Cresols and Hydrogen Peroxide in the Presence of Ferrous Sulphate 132

Yoshitaro TAKAYAMA: Studies on Amino-acids and Related Compounds. IX. Electrolytic Oxidation of Proline and γ-Amino-butyric Acid 138

Sin'iti KAWAI and **Noboru SUGIYAMA**: Synthesis of β, γ-Dihydroxypropyl-guanidine 141

Shin-ichi SAKO: 4,5-Bis-(*m*-aminophenyl)-carbazole 144

Harusada SUGINOME und **Sumio UMEZAWA**: Synthetische Versuche in der Selenophengruppe. I. Einwirkung von Chlor und Brom auf Selenophen 157

Kojiro SAITO and **Harusada SUGINOME**: On the Alkaloids of White Hellebore. II. Isolation of Alkaloids from the So-called Resinous Matters 168

Kojiro SAITO, Harusada SUGINOME, and **Michio TAKAOKA**: On the Alkaloids of White Hellebore. III. Experiments on the Constitution of Jervine 172

Teruko NAKAMURA: A New Bacterioxanthophyll, the Yellow Pigment of *Sarcina lutea*. (Preliminary Report.) 176

Nenokichi HIRAO: Synthesis of 4-Hydroxy-3-ethoxy-1-allyl-benzene from 4-Hydroxy-3-methoxy-1-allyl-benzene (Eugenol) 179

Mosuke HAYASHI, Sinzo TSURUOKA, Ikuo MORIKAWA, and **Hirochika NAMIKAWA**: Studies on the Derivatives of Benzoylbenzoic Acids 184

Kenji IWAMOTO: On the Derivatives of Anthrahydroquinone Disulphuric Acid Esters. I. Synthesis of Some Azo-Compounds . . . 201

Tsuneharu TANNO: Über die katalytische Hydrierung von Rohrzucker. I. Hydrierung von Rohrzucker mit reduziertem Nickel als Katalysator 204

Shiro AKABORI und Takeo KANEKO: Synthese von Imidazolderivaten aus α-Aminosäuren. III. Synthese von zwei höheren Homologen des Histamins 208

Shiro AKABORI und Shinji NUMANO: Synthese von Imidazolderivaten aus α-Aminosäuren. IV. Eine neue Synthese von Histamin 214

Toshio HOSHINO und Kiyoshi TAKIURA: Über die Synthese von Alkoxy- und Oxy-carbazole 218

Toshio HOSHINO und Kenya SHIMODAIRA: Über die Synthese des Bufotenin-methyl-äthers (5-Methoxy-*N*-dimethyl-tryptamin) und Bufotenins. (Synthesen in der Indol-Gruppe. XV.) 221

Keisuke YAMADA, Tadao NOGUCHI, and Koichi OIWA: Studies on Quinoxaline Colours 225

Munio KOTAKE and Tadahiro MITSUWA: Studies on the Structure of Strychnine. III. Strychninolone and its Derivatives 231

Tetsutaro TADOKORO: Influences of Hydrogen-acceptor on Fucose Fermentation by *Aspergillus oryzae* 239

Hiroaki KADOWAKI: New Compounds of Urea-formaldehyde Condensation Products 248

Terutaro OGATA: Über Cyaninfarbstoffe. VIII. Eine neue Synthese von 8-Methyl-trimethinthiocyanin-derivaten und über die Reaktionsfähigkeit der 8-Methylgruppe 262

Miss Chika KURODA: The Constitution of Awobanin and Awobanol, the Colouring Matter of Awobana and its Co-pigment 265

Chika KURODA and Mizu WADA: The Constitution of Natural Colouring Matters, Kuromamin, Shisonin, and Nasunin 272

Masuo MURAKAMI und Tôsi IRIE: Über ein Umlagerungsprodukt des Fukugetins (Fukugenetin) 288

Shin-ichiro FUJISE und Mitsuo IWAKIRI: Über die Stereoisomerie des 6-Methyldekahydrochinolins. (Vorläufige Mitteilung.) . . . 293

Tetsuo NOZOE: Über die Farbstoffe im Holzteile des "Hinoki"-baumes. I. Hinokitin und Hinokitiol. (Vorläufige Mitteilung.) . 295

Kunihiko SUMINOKURA: Über die Laccase des Japanischen Lacks. II. Über die Reagierbarkeit der Laccase gegen Polyphenole und Diamine 299

Eijiro OGAWA: The Exchang Reactions between Heavy Water and Hydrogen Compounds 310

No. 4. APRIL.

Kichimatsu MATSUNO and Kwan HAN: Studies of the Raman Effect of Organic Substances. V. Raman Effect of Homocyclic Compounds 321

Kôiti MASAKI: The Normal Frequencies of Vibration of Benzene Compounds in the Ultraviolet Absorption 346

Kozo HIROTA and Go OKAMOTO: Interchange Equilibrium between Acetylene and Heavy Water 349

No. 5. MAY.

Yuichi NAKATSUKA und Hirosi IINUMA: Versuche zur Aktivierung von Komplexsalzen, die ein durch Bindung an das Zentralatom entstandenes asymmetrisches Stickstoffatom enthalten 353

Yuichi NAKATSUKA und Hirosi IINUMA: Beiträge zur Kenntnis der komplexchemischen Ringsysteme mit Para-Bindung. I. *p*-Oxybenzaldehyd-*o*-phenylendiimin- und Vanillin-*o*-phenylendiiminkupfer 358

Yojiro TSUZUKI: Synthese einiger Brückenderivate der Weinsäure durch Acetalisierung ihrer Ester mit Aceton, Acetaldehyd und Formaldehyd 362

Eijiro OGAWA: The Exchange Reactions between Heavy Water and Amino Acids and Carbohydrates 367

Buhei SAKURAI: Electrolytic Reduction of Pyrrole 374

Ei-ichi IWASE: Zur Kenntnis der Fluoreszenz von japanischen Hyaliten im ultravioletten Lichte. II. Mitteilung 377

No. 6. JUNE.

Ryuzaburo NODZU and Ryozo GOTO: The Action of Weak Alkalies upon Glucose. I 381

Haruomi ÔEDA: Action of Liquid Ammonia upon Acetone-compounds of *α*-Hydroxy-acids 385

Kunio OKAHARA: Über die in den Blättern von *Ficus Carica* enthaltenen Bestandteile 389

Sei-ichi UENO and Ryosei KOYAMA: On the Occurrence of Many New Constituents in the Unsaponifiable Matter of Sperm Blubber Oil 394

Noriyoshi MORITA und Toshizo TITANI: Erzeugung des leichten Wassers und Bestimmung der Deuterium-Konzentration im normalen Wasser 403

Noriyoshi MORITA und Toshizo TITANI: Über den Unterschied in der Isotopenzusammensetzung von Luft- und Wassersauerstoff und den elektrolytischen Trennfaktor von Sauerstoffisotope . . . 414

Noriyoshi MORITA und Toshizo TITANI: Über den Einfluss des Dichteunterschieds zwischen Luft- und Wassersauerstoff auf die Versuchsergebnisse von Sauerstoff- und Wasserstoffisotope . . . 419

Eijiro OGAWA: The Mechanism of the Isotopic Exchange Reactions 425

Eijiro OGAWA: The Isotopic Separation of Oxygen, Chlorine, Bromine, and Nitrogen by the Chemical Methods 428

Kazuo YAMASAKI: Über die katalytischen Oxydationswirkung der Metallkomplexverbindungen. XI. Katalytische Oxydation in schwerem Wasser 431

Yoshiyuki URUSHIBARA and Toshio ANDO: The Formation of Cholestanedione-(3,6) from Cholestenone Dibromide and from Δ^4- and Δ^5-Cholestenones 434

No. 7. JULY.

Sei-ichi UENO and Chizuo YONESE: On the Occurrence of New Highly Unsaturated Fatty Acids, $C_{26}H_{40}O_2$ and $C_{26}H_{42}O_2$, in Tunny Oil 437

Naoyasu SATA: Über die Kolloidsynthese durch Dampfexplosionen und die kolloidchemischen Untersuchungen der durch diese Methode hergestellten dispersen Systeme 443

Ryoichi MATSUDA: The Electrolytic Formation of Sodium Perborate. Part I 456

Masao HARADA und Toshizo TITANI: Isotopenaustausch zwischen Wasser und einigen organischen Verbindungen 465

Ei-chi IWASE: Über die Verteilung des Lumineszenzträgers im Gipskristall 475

No. 8. AUGUST.

Naoyasu SATA: Über die Kolloidsynthese durch Dampfexplosionen und die kolloidchemischen Untersuchungen der durch diese Methode hergestellten dispersen Systeme. (*Fortsetzung.*) 481

Kyôji KINOSHITA: On the Changes of Weight of the Electrodes of the Lead-Acid Storage Cell in the Course of Discharge 504

Ei-ichi IWASE und Takehiro KURONUMA: Zur Lumineszenz des Calcits. I. Das Fluoreszenzspektrum japanischen Calcits im ultravioletten Lichte 513

Ei-ichi IWASE: Zur Lumineszenz des Calcits. II. Thermolumineszenzspektren japanischer Calcite 523

Ei-ichi IWASE: Zur Lumineszenz des Calcits. III. Änderung der Fluoreszenzspektren von Calciten durch vorheriges Erhitzen . . . 528

Jitsusaburo SAMESHIMA and Tsunetaka SASAKI: Studies of Monomolecular Films by the Ripple Method. I 539

Tsunetaka SASAKI and Jitsusaburo SAMESHIMA: Studies of Monomolecular Films by the Ripple Method. II 547

San-ichiro MIZUSHIMA, Yonezo MORINO und Go OKAMOTO: Ramanspektrum von Deuteroäthanol 553

Masao HARADA und Toshizo TITANI: Der Isotopenaustausch zwischen Anilinchlorhydrat und schwerem Wasser. (Vorläufige Mitteilung.) 554

No. 9. SEPTEMBER.

Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI: The Nitrile-esters of 2-Methylpropene-1,1,3,3-tetracarboxylic Acid 557

Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI: The Electrolytic Dissociation of 1, 1, 3, 3-Tetracyano-propene and 1,1,3,3-Tetracyano-2-methylpropene 569

Kichimatsu MATSUNO and Kwan HAN: Studies on the Raman Effect of Organic Substances. VI. Raman Effect of Sesquichamene and Some Other Terpenes 576

Yojiro TSUZUKI: Optical Rotatory Dispersion of Some Bridged Derivatives of Alkyltartrates 586

Toshizo TITANI und Kenzo OKABE: Über den Gehalt des Salzwassers aus Petroleumquellen an schwerem Wasser. I 593

Naoyasu SATA: Über die Kolloidsynthese durch Dampfexplosionen und die kolloidchemischen Untersuchungen der durch diese Methode hergestellten dispersen Systeme. (*Fortsetzung und Schluss.*) . . . 598

J. HORIUTI and Y. SAKAMOTO: Isotopic Interchange Reaction between Chloroform and Water 627

No. 10. OCTOBER.

Yuichi NAKATSUKA: Über Kobaltiammine, die quartäre Ammoniumbasen koordinieren 629

Sei-ichi UENO and Masayoshi IWAI: On the Oil of Hokke (*Pleurogrammus monopterygius*, Pallas), with Special Reference to the Occurrence of New Highly Unsaturated C_{23}-Fatty Acids 643

Ryoichi MATSUDA and Teruichi NISHIMORI: The Electrolytic Formation of Persulphate. Part II 650

Jitsusaburo SAMESHIMA, Meiji KIDOKORO and Hideo AKAMATU: Studies on the Oiliness of Liquids. I. Measurements of the Static Friction Coefficients 659

B. TAMAMUSHI und H. UMEZAWA: Über die heterogene Reaktionskinetik der Umwandlung von Dibrombernsteinsäure in Monobromfumarsäure 667

Kyozo ARIYAMA: A Theory of the Negative Adsorption of Debye-Hückel Electrolyte 687

Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI: The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. I 692

Noriyoshi MORITA und Toshizo TITANI: Über den Gehalt der Kohlenhydrate an schwerem Sauerstoff. (Vorläufige Mitteilung.) 695

San-ichiro MIZUSHIMA, Yonezo MORINO und Go OKAMOTO: Ramanspektrum von Deuteromethanol 698

No. 11. NOVEMBER.

Kwan HAN: Studies on the Raman Effect of Organic Substances. VII. Raman Effect of Furane Derivatives 701

Kôiti MASAKI: The Absorption Spectra of Nitroglycerine 712

Yuzuru OKUDA and Kitaro KATAI: Chemical Studies on Canned Meats. II. On the Contents of Gases and Metals in Stored Cans. 715

Yuzuru OKUDA and Kitaro KATAI: Chemical Studies on Canned Meats. III. Carbon Dioxide and Hydrogen Gases produced at Canning and in Storage 718

Ryutaro TSUCHIDA: Spectrographic Methods of Studying Unstable Compounds. II. The Aquotization of Trans-dichlorotetrammine Cobaltic Chloride in Aqueous Solutions. 721

Yoshiyuki TOYAMA and Tokuzo ISHIKAWA: Dihydroxystearic Acid in Castor Oil 735

Yoshiyuki TOYAMA and Tomotaro TSUCHIYA: The Highly Unsaturated Acids in Sardine Oil. XII. A Further Experiment on the Separation of Octadecatrienoic Acid $C_{18}H_{30}O_2$ 741

Yoshiyuki TOYAMA and Tomotaro TSUCHIYA: The Highly Unsaturated Acids in Sardine Oil. XIII. Oxidation of Methyl Clupanodonate with Potassium Permanganate in Acetone Solution 745

Yoshiyuki TOYAMA and Tomotaro TSUCHIYA: The Highly Unsaturated Acids in Sardine Oil. XIV. Oxidation of Potassium Clupanodonate with Potassium Permanganate in Aqueous Solution 751

Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI: The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. II. Further Experiments on the Effects of Ferromagnetic Catalysts 754

Yoshiyuki URUSHIBARA and Toshio ANDO: The Formation of an Isomeride of Neoergosterol by the Pyrolysis of Ergopinacone . . . 757

No. 12. DECEMBER.

Nobutoshi ICHIKAWA: Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. I. The Isolation of Shonanic Acid and its General Properties 759

Takeo ITO, Harusada SUGINOME, Kiyoshi UENO und Shigeto WATANABE: Über die Farbstoffe des Goldröschens, *Kerria japonica*, DC 770

Sumio UMEZAWA: Synthetische Versuche in der Selenophen-Gruppe. II. Nitrierung und Sulfonierung 775

Kunisaburo TAMURA: Studies on the Structure of Asebotin, a Component of *Andromeda japonica* Thumb 781

Ryutaro TSUCHIDA and Shin KASHIMOTO: The Third Absorption Bands of Co-ordination Compounds. I. $[Co(NH_3)_4ClNO_2]Cl$ and $[Co(NO_2)_6]Na_3$ 785

Hideo AKAMATU and Jitsusaburo SAMESHIMA: Studies on the Oiliness of Liquids. II. Friction Coefficients of the Films of Mono- and Poly-molecular Layers 791

Tunetaka SASAKI: On the Stability of Foam 797

Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI: The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. III. A Contribution to the Elucidation of the So-called Peroxide Effect 798

Yoshiyuki URUSHIBARA and Toshio ANDO: The Photochemical Dehydrogenation of 7-Dehydro-cholesterol 802

Author Index to Volume 11 803

Corrections to Volume 11 809

BULLETIN OF THE
CHEMICAL SOCIETY OF JAPAN

THE ELECTROLYTIC FORMATION OF PERSULPHATE. PART I.

By Ryoichi MATSUDA.

Received September 16th, 1935. Published January 28th, 1936.

Various studies have been done on the electrolytic formation of persulphate, but most of them seem to be unsystematic for reason that their primary purpose is the determination of the best conditions for the manufacture of persulphate, the theoretical side of the problem being necessarily neglected.

M. Berthelot[1] considers that the formation of persulphuric acids is a process of oxidation by the hydrogen peroxide formed at the anode. K. Elbs and O. Schönherr[2], on the other hand, attribute this formation to two discharged HSO_4-ions united together in an analogous manner to the formation of the chlorine molecule by the union of two discharged Cl-ions when hydrochloric acid is electrolysed. Then again, F. Foerster[3], in his book, states that the oxidation of SO_4-ions by anodic oxygen is responsible for the persulphate formation, and gives a complicated interpretation of the mechanism of the anodic reactions.

When the present writer[4]gave explanations for Kolbe's reaction, the electrolytic oxidation of fatty acids, on the basis of the peroxide theory, he suggested, from the result of electrolysis of dilute solutions of ammonium and potassium sulphates, that the electrolytic formation of the persulphate might be similarly explained.

Experimental.

A spiral of thin Pt-wire was used as the anode, immediately after being treated according to the method employed by Goard and Rideal[5], and rotated at the center of a porous cylinder, which stood at the center of a beaker and made the anode chamber. The cathode was also a spiral Pt-wire placed

(1) *Compt. rend.*, **90** (1880), 269; *ibid.*, **112** (1891), 1418.
(2) *Z. Elektrochem.*, **1** (1894), 417.
(3) "Elektrochemie wässeriger Lösungen," 1923.
(4) *Complete Abst. Japanese Chem. Literatures* (*Nippon Kwagaku Soran*), 2nd Series, **6** (1932), 85B.
(5) *Trans. Faraday Soc.*, **19** (1924), 740.

against the inner wall of the beaker. The anolyte, 90.0 c.c. at the commencement, was kept at 16-18°C. by circulating water through a glass tubing immersed in the cylinder. The anolyte was stirred by the rotation of the anode. The same amount of electricity, 828 coulombs, was supplied in each electrolysis.

The analysis of the electrolysed solution was performed as follows: a 40.0 c.c. portion out of the anolyte which was about 89.5 c.c. after electrolysis in each case was mixed with a sodium acetate solution sufficient for making it acid with regard to acetic acid and then titrated with potassium sulphite with iodine as indicator. This titration gave the amount of Caro's acid present. Another 40.0 c.c. portion was treated with a ferrous sulphate solution at about 50°C., being adequately acidified with sulphuric acid when necessary and was then back-titrated with potassium permanganate, which gave the total amount of the peroxidic oxygen, i. e. persulphuric acid, Caro's acid and hydrogen peroxide. The potassium sulphite solution was prepared with potassium pyrosulphite[6] and was stored under nitrogen. Coloured sulphate solutions, such as those of Fe and Cu, could not be titrated with the sulphite solution. For the estimation of the total peroxidic oxygen of such solutions potassium bichromate was employed instead of permanganate, with barium diphenyl-sulphonate as indicator.

Experiment 1. Influences of Current Density and $H^{\cdot}$-Concentration. This was rather a repetition of what had been done by Elbs and Schönherr[7]. A 10 N sulphuric acid free from ammonium sulphate was denoted by (0 : 10), and a solution of 2 and 8 N respectively with regard to the sulphate and sulphuric acid by (2 : 8), and so on. The solutions employed here were (0 : 10), (2 : 8), (4 : 6), (6 : 4), (8 : 2), and the saturated solution of ammonium sulphate which was 7.88 N and contained no free sulphuric acid. The current efficiencies are shown in Tables 1 and 2. No hydrogen peroxide was detected in any of above cases with titanium sulphate. Amounts of Caro's acid were small in all cases, although they increased with total amount of peroxidic oxygen, which itself increased with the rise of the current density.

The highest current efficiency with regard to this peroxydic product was obtained in the case of the saturated solution of ammonium sulphate with the current density 1.6 amp./cm.^{2}, which amounted to 2.5%. Therefore, nothing conclusive can be deduced out of the current efficiency with respect to Caro's acid.

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(6) F. Foerster, *Z. physik. Chem.*, **110** (1924), 476. S. Glasstone and A. Hickling, *J. Chem. Soc.*, **1933**, 829.

(7) *Z. Elektrochem.*, **2** (1895), 245.

Table 1. Current Efficiencies with Regard to Caro's Acid.

Solution \ Current density	0.05 amp./cm.^{2}	0.10	0.20	0.40	0.80	1.60
(0:10)	0.3%	0.3	0.4	1.4	2.2	2.4
(2: 8)	0.7	0.5	1.2	1.1	1.7	2.5
(4: 6)	0.6	0.6	0.7	0.9	0.9	1.0
(6: 4)	0.4	0.5	0.6	0.8	1.4	1.8
(8: 2)	0.8	1.6	1.6	1.9	0.8	1.4
The saturated solution of $(NH_4)_2SO_4$	2.2	2.3	0.9	1.1	1.9	2.5

Table 2. Current Efficiencies with Regard to the Total Peroxidic Oxygen.

Solution \ Current density	0.05 amp./cm.^{2}	0.10	0.20	0.40	0.80	1.60
(0:10)	2.2%	3.3	4.6	21.4	45.8	63.7
(2: 8)	18.0	28.6	41.5	56.3	76.9	87.5
(4: 6)	35.5	38.9	56.3	63.9	78.2	74.5
(6: 4)	49.5	56.7	69.0	74.4	83.4	83.1
(8: 2)	57.3	60.6	74.4	81.1	87.2	92.0
The saturated solution of $(NH_4)_2SO_4$	59.6	60.5	68.9	84.2	82.4	89.0

Increase of the current density was favourable, in general, to the anodic oxidation, and the effect of the increase on the current efficiency with respect to the total peroxidic oxygen was the greatest in the case of (0:10) among the six solutions; the more concentrated was the solution with regard to ammonium sulphate, the less marked was the effect. When part of the free sulphuric acid was replaced by the sulphate, there were more OH-ions brought into existence as the result of H- and SO_4-ions uniting themselves together to form acid sulphate.

The difference of the current efficiencies generally observed between (0:10) and (2:8) was greater than any other succeeding pairs. This is because the difference of OH′-concentrations was presumably the greatest in this case. When solutions were more concentrated with respect to ammonium sulphate, for instance (8:2), the OH′-concentrations were considerably greater than that of (0:10), so that fairly high current efficiencies were obtainable even with the smallest current density (Fig. 1). One of the highest current efficiencies was obtained with the saturated solution of am-

monium sulphate in spite of its comparatively smaller concentration and also of its being neutral at the beginning. If this solution had been so concentrated as 10 N, it is very probable that its current efficiency might have been greater than any other.

Elbs and Schönherr's view can hardly account for these facts, but OH-ions discharged at the anode seem to the writer to play an important rôle in the persulphate formation. S. Glasstone and A. Hickling[8] proposed that hydrogen peroxide is the effective oxidizing agent in anodic oxidation of certain inorganic salts. In the present case, however, it is not the primary concern whether hydrogen peroxide or nascent oxygen is the oxidizing agent, though for convenience's sake the latter is assumed to be the case. It is evident, anyhow, that increase of OH' is favourable to the persulphate formation in this experiment when solutions with the same total concentration of the sulphate radical are electrolysed.

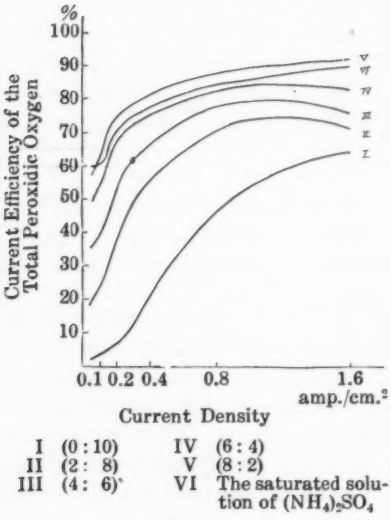


Fig. 1.

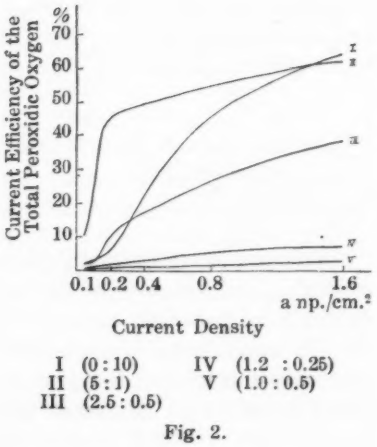


Fig. 2.

Experiment 2. Influence of Concentration. A solution which was 5 and 1 N with regard to ammonium sulphate and sulphuric acid respectively was denoted (5:1) and so on. Four solutions, (5:1), (2.5:0.5), (1.25:0.25), and (1.0:0.5), were electrolysed with the same current densities as before, and the current efficiencies of these solutions are shown in Fig. 2.

(8) *J. Chem. Soc.*, **1932**, 2345, 2800; *ibid.*, **1933**, 829.

Differences of current efficiencies of above solutions can easily be understood from the view point of concentration. That the current efficiencies of (0 : 10) of Experiment 1 and (5 : 1) of this experiment were alike is noteworthy, considering the far greater concentration of the former with respect to the sulphate radical. This point can be explained by the fact that the latter had greater OH′-concentration. The difference between (1.25 : 0.25) and (1.0 : 0.5), both of which had the same total concentration of the sulphate radical, is similarly explicable.

Experiment 3. Influences of Various Cations. A 7 N sulphuric acid solution and those which were 2 and 5 N respectively with regard to sulphate and sulphuric acid were electrolysed. The copper solution which was obtained by saturating 5 N sulphuric acid with copper sulphate was nearly normal with regard to the sulphate. The current efficiencies of these solutions are shown in Table 3 and Fig. 3.

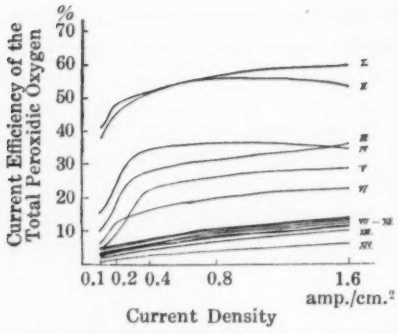
Table 3. Current Efficiencies with Regard to the Total Peroxidic Oxygen of Solutions which were 2 and 5 N Respectively with Regard to the Corresponding Sulphate and Sulphuric Acid.

Current density / Sulphate	0.10 amp./cm.^{2}	0.20	0.40	0.80	1.60
K_2SO_4	36.4%	46.0	51.3	59.2	60.1
$(NH_4)_2SO_4$	10.4	17.6	24.4	30.8	36.2
Na_2SO_4	3.3	8.5	22.2	26.2	27.8
H_2SO_4	3.2	3.8	4.3	8.0	12.3
$MgSO_4$	1.0	1.8	6.3	8.3	12.0
Li_2SO_4	0.6	1.5	3.8	4.8	10.3
$Al_2(SO_4)_3$	3.5	4.8	6.3	9.3	12.6
$CdSO_4$	1.0	1.8	4.6	8.6	10.9
$Fe_2(SO_4)_3$	2.3	2.6	4.3	4.8	6.5
$CuSO_4$	3.0	4.0	6.4	7.1	9.2
$ZnSO_4$	1.0	1.0	1.8	3.1	4.7

These sulphates can be classified into two according to the current efficiencies of corresponding solutions. Sulphates of K, NH_4, and Na are one class and the others, i. e. those of Li, Mg, Zn, Fe(ferric), Al, Cu, and Cd, are the other.

One characteristic property common to the three former sulphates is the capability of forming the acid sulphate. Its formation which causes the

increase of OH′-concentration can possibly account for higher current efficiencies of these solutions. Why, then, did the potassium sulphate solution give the highest current efficiencies? Let the writer explain. According to A. Kailan and E. Leisek[9] different alkali metal ions have different effects on persulphate decomposition. To verify their result, 20 N sulphuric acid was electrolysed for half an hour with a current density of 0.8 amp./cm.^{2} To each of three 10 c.c. portions of the anolyte after electrolysis was added potassium, ammonium, and sodium sulphates respectively enough to make the solution normal with regard to the corresponding sulphate. These three solutions as well as a blank one were titrated, after allowing them to stand for $1^1/_2$ hours at 85–90°C. with frequent stirring.



I 2 N K_2SO_4, 5 N H_2SO_4
II 1 N K_2SO_4, 1 N $ZnSO_4$, 5 N H_2SO_4
III 2 N $(NH_4)_2SO_4$, 5 N H_2SO_4
IV $^1/_2$ N K_2SO_4, $1^1/_2$ N $ZnSO_4$, 5 N H_2SO_4
V 2 N Na_2SO_4, 5 N H_2SO_4
VI 1 N $(NH_4)_2SO_4$, 1 N $ZnSO_4$, 5 N H_2SO_4
VII–XII 2 N sulphate, 5 N H_2SO_4; sulphates being those of H_2, Mg, Li, Al, Cd and Fe(III)
XIII 1 N $CuSO_4$, 5 N H_2SO_4
XIV 2 N $ZnSO_4$, 5 N H_2SO_4

Fig. 3.

The total peroxidic oxygen of the blank, K_2SO_4, $(NH_4)_2SO_4$, and Na_2SO_4 solutions were respectively 35.0, 19.7, 34.2, and 4.9% of the theoretical current efficiency. Thus Na-ions proved to be the most effective, K-ions coming next, and NH_4-ions being the least on persulphuric acid decomposition.

Furthermore, different solubilities of various persulphates have to be taken into consideration. It can be assumed that the region of the anolyte which is very close to the anode is exceedingly concentrated with respect to persulphuric acid, compared with the bulk of the solution; consequently its decomposition by cations is extraordinarily vigorous there. The solubilities of $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ at 0°C. are 1.73 and 36.7 parts respectively in 100 parts of the saturated solution. This vast difference of solubilities of these two persulphates may be the probable cause, by which the decomposing effect of cations was more than compensated, and which gave rise to the greatest current efficiency in the case of potassium sulphate.

(9) *Monatsh.*, **50** (1928), 403.

The reason why the other sulphates did not have any marked effect (except a slightly negative one with Zn-salt) remains to be investigated. The effect of replacing half the amount of potassium in the K_2SO_4 solution with zinc and the corresponding case of $(NH_4)_2SO_4$ (Fig. 3) can be explained in the same way as above. In the case of the solution ($^1/_2$N K_2SO_4, $1^1/_2$N $ZnSO_4$, 5N H_2SO_4) the influence of Zn-salt was more marked.

It is interesting to examine whether there was any catalytic effect of cations on persulphate decomposition in Experiment 1. The cations concerned therewith were $H^{\cdot}$ in (0:10) and $NH_4^{\cdot}$ and $H^{\cdot}$ in the other five solutions. As mentioned above, $(NH_4)_2SO_4$ added to 20N sulphuric acid which had been electrolysed caused more persulphate to be decomposed than in the blank solution, hence, $H^{\cdot}$ had, if any, less effect on persulphate decomposition than $NH_4^{\cdot}$. Therefore, these five solutions of Experiment 1 which contained ammonium sulphate were more affected, but not less certainly, by cations on the decomposition in question than 10N sulphuric acid. Nevertheless, the more concentrated the solutions were with regard to $NH_4^{\cdot}$, the greater were the current efficiencies.

Summary.

1. Sulphuric acid and ammonium sulphate solutions were electrolysed in order to see the influences of the current density and OH′-concentration.

2. Influence of various cations, $H^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$, $Na^{\cdot}$, $Li^{\cdot}$, $Mg^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Cu^{\cdot\cdot}$, and $Cd^{\cdot\cdot}$, was studied and some were explained to have connexion with persulphate formation.

3. A new suggestion was made that OH′ plays an important rôle in persulphate formation, and this suggestion will clearly explain the results of the present investigation which may otherwise be obscure.

The author wishes to thank Dr. S. Glasstone, F.I.C., of the University of Sheffield for his deep interest in the present investigation.

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A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. XII.

By Tetsuya ISHIKAWA and Toshitomo BABA.

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Mixtures showing minima in the viscosity versus concentration curves. Mixtures of alcohols with benzene have been treated by several investigators with recent views to the molecular complexity of liquids. Despite that the mixture of ethyl alcohol with benzene has an eutectic point on the freezing point curve, the molecular weight of the alcohol in benzene as determined by the freezing point method has been found abnormally high for concentrations above 0.278 mol. % alcohol according to Gibbons[1] or 0.383 mol. % alcohol according to Peterson and Rodebush.[2] The mean molecular weight calculated from Gibbons's data if it is taken at the concentration range from 1.8 to 35.5 mol. % is 170 or 3.7 times the formal molecular weight. Such an anomalous phenomenon of association as observed in the case of the alcohol in benzene has been quite recently criticized by Müller and Mortier.[3] The van Arkel association[4] which signifies that the molecular polarization P of dipole substances dissolved in a solvent polar or non-polar is simply related to the concentration by van Arkel's formula

$$P = \frac{4\pi}{3} n\left(\alpha + \frac{\mu^2}{3kT + cn\mu^2}\right)$$

(α is the optical polarization, n the number of dipole per c.c., μ the dipole moment, k the Boltzmann constant, and c a constant) does not fit for the case in question. Substances with van Arkel's association scarcely indicate molecular complex cryoscopically and ebullioscopically as it is a well known fact that alcohols give normal molecular weights in dilute aqueous solutions. They point out that although propyl alcohol appears to obey the above rule at very low concentration, yet the constant c thereby gives about 60, whereas the normal value lies between 1.1 and 1.8, and conclude that even at extremely high dilution the reciprocal action of the alcohol molecules seems to

(1) W. A. Gibbons, *J. Phys. Chem.*, **21** (1917), 48.
(2) J. M. Peterson and W. H. Rodebush, *J. Phys. Chem.*, **32** (1928), 709.
(3) F. H. Müller and P. Mortier, *Physik. Z.*, **10** (1935), 371.
(4) A. E. v. Arkel and J. L. Snoek, *Trans. Faraday Soc.*, **30** (1934), 707.

become greater than the separating force of the solvent and such effect is attributed to the anomalous position of the dipole within the alcohol molecules.

Gundermann[5] observes that the pairs of butyl alcohol-benzene and especially ethyl alcohol-benzene do not obey the theory of Debye which tells that the dielectric constant of liquids decreases as the square of the applied voltage. As to the former pair the decrease of dielectric constant with voltage is qualitatively understood from the Debye theory, but the latter pair behaves anomalously in such a manner that the effect indicates relatively high value at low concentration of the alcohol, but too low at high concentration, the pure alcohol, however, showing little effect against field intensity. He attributes this to the association of the alcohol molecules in benzene solution.

The anomalous behaviour of benzene towards alcohols has also been known in the measurement of infra-red absorption spectra. Freymann[6] notices that in the mixtures of butyl alcohol and ethyl alcohol with benzene the characteristic frequency band of OH-group at 0.9631 μ shifts intensively to 0.9778 μ, and that the same band of alcohols also shifts to longer wave in the dilution of the alcohols with benzene, but that such phenomenon is scarcely observed with other solvents.

The viscosity of mixtures of benzene with alcohols, especially with ethyl and propyl alcohols studied by Dunstan[7], indicates a distinct minimum against the composition in each system. No adequate reason has been given for binary liquid mixtures which exhibit minima in the viscosity versus concentration curves. If we take an analogy to the phenomena of some inorganic salts such as NH_4-, K-, Rb-, and Cs-halides in consideration,[8] the viscosity minimum would be elucidated by the dissociation of alcohol molecules as Dunstan supposes, but such opinion is not only opposite to the recent view above cited, but also gives unsatisfactory results in actual calculation, since midway of the curves cannot be expressible by such method of calculation in which two solutional viscosities of both components must be postulated at the same time. Therefore, so far as the present knowledge of alcohols-benzene mixtures is concerned, we are reduced to assume that the anomalous change of association of alcohol molecules occurs in benzene solution, a change tends probably to greater association.

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(5) H. Gundermann, *Ann. Physik.*, [5], **6** (1930), 545.

(6) R. Freymann, *Compt. rend.*, **193** (1932), 923.

(7) A. E. Dunstan, *J. Chem. Soc.*, **85** (1904), 817; **87** (1905), 11; *Z. physik. Chem.*, **49** (1904), 590.

(8) T. Ishikawa and T. Baba, this Bulletin, **10** (1935), 153.

In this series of papers[9] the authors have developed the Ishikawa formula for the viscosity of binary mixtures standing on the fundamental hypothesis that the associations of both components are invariant throughout the concentration when no chemical change on their mixing. A reflection shall be given on this point.

If there happens some anomalous (increasing or decreasing) change of association in one component, say, component 2 in its greatest dilution with component 1 where the quantity of component 2 is quite enough to change its original association a_2 into a'_2 statistically, component 2 in the opposite case in quantity may also suffer change in association more or less, the degree of which, however, is not always the same in both the extremities, say, a_2 tends statistically to a''_2 in this case. If such is the case, the viscosity change with composition between these extremities may be expressible by the following formula:

$$\eta = \frac{\eta_1 k_1 a_1 (1-z_m)}{k_1 a_1 (1-z_m) + k_2 a'_2 z_m} + \frac{\eta_2 k_2 a''_2 z_m}{k_1 a_1 (1-z_m) + k_2 a''_2 z_m}$$

$$= \frac{\eta_1}{1 + K' \dfrac{z_m}{1-z_m}} + \frac{\eta_2}{1 + K'' \dfrac{1-z_m}{z_m}}$$

in which $K' = \dfrac{k_2 a'_2}{k_1 a_1}$ and $K'' = \dfrac{k_1 a_1}{k_2 a_2''}$.

It is easily understood by simple calculation that the necessary condition under which η as expressed by the above formula takes a minimum is $K'K'' > 1$.

Provided that the anomalous behaviour of benzene towards alcohols attributes wholly to the change of association of alcohols as defined above and to no further interactions between both the component molecules, viscosity curves between the two extremities must be completely expressible by this formula.

The viscosity data for these mixtures are adopted from the studies of Dunstan, Fischler, and Bhide and Watson.[10] The calculated values are listed in the third column in each table from Tables 1 to 4, and how they are compared with observed values is clearly seen from Fig. 1, in which the curves are all traced by use of the calculated values, putting the viscosities of benzene at given temperatures as unity.

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(9) T. Ishikawa, this Bulletin, **4** (1929), 5, 25, 149, 288; **5** (1930), 47, 117; **8** (1933), 280, 293; **9** (1934), 155; **10** (1935), 153, 248.

(10) A. E. Dunstan, *loc. cit.* J. Fischler, *Z. Elektrochem.*, **19** (1913), 126. B. W. Bhide and H. E. Watson, *J. Chem. Soc.*, **1927**, 2101.

For the system ethyl alcohol (2)-benzene (1) the K' (1.754) thus obtained is, as recent views demand, much greater than the normal K (0.466) as calculated on the assumption that no change of association occurs on mixing the two liquids, their ratio giving 3.76. This value is quite coincident with the value 3.7 as the abnormal value of the association of the alcohol already explained at the begining of this paper.

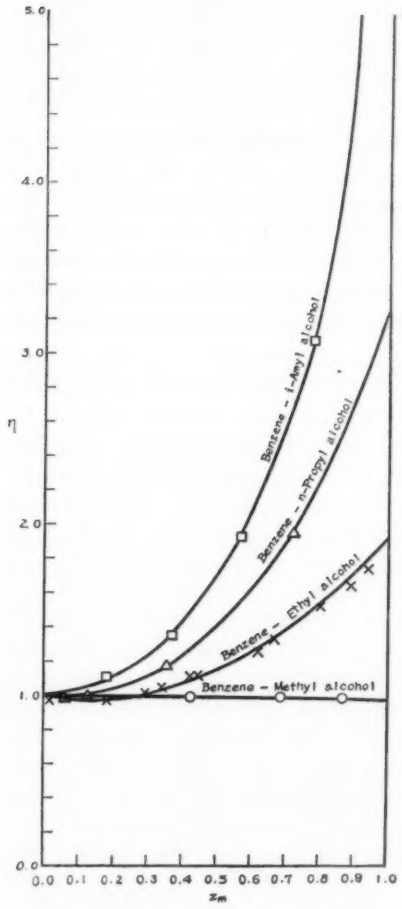

Fig. 1.

Table 1. Benzene—Methyl alcohol, 25°C. (Fischler).

z_m	η obs.	η calc.
0.0000	0.005758	—
0.4235	0.005723	0.005720
0.6879	0.005684	0.005681
0.8684	0.005645	0.005643
1.0000	0.005608	—

$K' = 0.619$, $K'' = 1.603$. $K'K'' = 0.99$.

Table 2. Benzene—Ethyl alcohol, 25°C. (Dunstan).

z_m	η obs.	η calc.
0.0000	0.005821	—
0.0192	0.005668	0.005778
0.1874	0.005669	0.005669
0.2927	0.005885	0.005840
0.3421	0.006071	0.005977
0.4267	0.006465	0.006287
0.4485	0.006514	0.006395
0.6205	0.007282	0.007398
0.6692	0.007758	0.007758
0.8067	0.008837	0.008956
0.8923	0.009545	0.009848
0.9475	0.01013	0.01048
1.0000	0.01113	—

$K' = 1.754$, $K'' = 1.453$. $K'K'' = 2.55$.

Table 3. Benzene—*n*-Propyl alcohol, 25°C. (Dunstan).

z_m	η_i obs.	η_i calc.
0.0000	0.005978	—
0.0631	0.005917	0.005934
0.1291	0.005989	0.005990
0.3554	0.007028	0.006952
0.7243	0.01167	0.01167
1.0000	0.01962	—

$K' = 1.701$, $K'' = 2.246$. $K'K'' = 3.82$.

Table 4. Benzene—*i*-Amyl alcohol, 30°C. (Bhide and Watson).

z_m	η_i obs.	η_i calc.
0.0000	0.00562	—
0.1813	0.00621	0.00607
0.3714	0.00760	0.00760
0.5707	0.0108	0.0108
0.7802	0.0173	0.0173
1.0000	0.0321	—

$K' = 1.712$, $K'' = 3.355$. $K'K'' = 5.74$.

For other systems the anomalies of the association of alcohols are not so great as that of ethyl alcohol, but their products $K'K''$'s still take greater values than unity, although K'''s seem to approach to their normal K's.

The anomalous change of molecular complexity of ethyl alcohol is also observed in viscosity determination with other solvents such as nitromethane, cyanobenzene, and allyl mustard oil.[11] With respect to these mixtures other physical properties to be needly explained are little known except that nitromethane has van Arkel's association.

Tables 5, 6, and 7 and Fig. 2 show the coincidence between the observed and calculated viscosities.

Table 5. Ethyl alcohol—Nitromethane (Wagner).

z_m	η_i obs.	η_i calc.
0.0000	1.0000	—
0.0579	0.9015	0.9043
0.1153	0.8210	0.8249
0.2290	0.7037	0.7042
0.4505	0.5704	0.5652
0.6518	0.5143	0.5143
0.8288	0.5003	0.5114
1.0000	0.5385	—

$K' = 2.231$, $K'' = 1.268$. $K'K'' = 2.83$.

Table 6. Ethyl alcohol—Cyanobenzene (Wagner).

z_m	η_i obs.	η_i calc.
0.0000	1.0000	—
0.0073	0.9958	0.9941
0.0147	0.9883	0.9880
0.0297	0.9784	0.9771
0.0607	0.9539	0.9560
0.1273	0.9210	0.9206
0.2703	0.8949	0.8823
0.3718	0.8785	0.8780
0.6346	0.9091	0.9264
1.0000	1.0768	—

$K' = 2.000$, $K'' = 0.925$. $K'K'' = 1.85$.

(11) J. Wagner, *Z. physik. Chem.*, **46** (1903). 867.

Table 7. Ethyl alcohol—Allyl mustard oil (Wagner).

z_m	η_i obs.	η_i calc.
0.0000	1.0000	—
0.0611	0.9237	0.9279
0.1275	0.8523	0.8551
0.2790	0.7331	0.7331
0.4810	0.6512	0.6349
0.6902	0.5995	0.5917
0.7769	0.5879	0.5879
1.0000	0.6100	—

$K' = 1.823$, $K'' = 1.221$. $K'K'' = 2.23$.

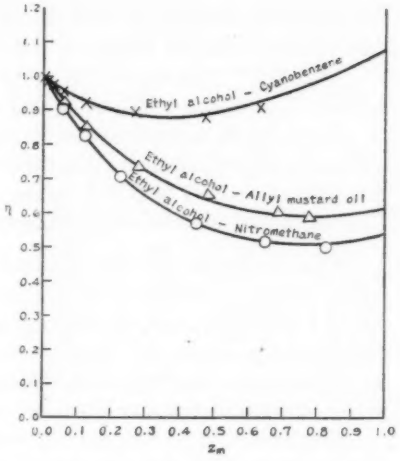

Fig. 2.

The mixture of acetic acid and benzene has been a subject in recent years for the same object of study as in alcohols-benzene mixtures. Bury and Jenkins[12] observe with a cryoscopic method that the molecular form of acetic acid in benzene is completely dimeric at all concentrations greater than ca 3 mol. % acetic acid. Beckmann and Liesche[13] obtain with an ebullioscopic determination that acetic acid in benzene is not completely dimeric, but partially suffers molecular dissociation to give 0.87 times the dimolecular weight for the mean value between 0.9 and 9.4 mol. % acetic acid. Dadieu and Kohlrausch[14] study the Raman effect of this mixture and of mixtures of acetic acid in other solvents such as ether, alcohol, and water, and point out that the deepest frequency 440 of acetic acid is markedly weakened in benzene solution, and moreover that

Table 8. Benzene—Acetic acid, 25°C. (Dunstan).

z_m	η_i obs.	η_i calc.
0.0000	0.005978	—
0.0355	0.005941	0.005965
0.1295	0.005907	0.005942
0.2289	0.005962	0.005960
0.2769	0.005969	0.005988
0.5822	0.006658	0.006637
0.7081	0.007341	0.007344
0.8666	0.008932	0.009007
1.0000	0.01174	—

$K' = 0.711$, $K'' = 3.108$. $K'K'' = 2.21$.

(12) C. R. Bury and H. O. Jenkins, *J. Chem. Soc.*, **1934**, 688.
(13) E. Beckmann and O. Liesche, *Z. physik. Chem.*, **92** (1917), 421.
(14) A. Dadieu and K. W. F. Kohlrausch, *Physik. Z.*, **31** (1930), 514.

the powerful frequency 1432 is replaced by two weak frequencies, these phenomena being not observed in other solvents.

Dunstan[15] who makes viscosity determinations on this mixture confirms a distinct minimum existing at 16.7 mol. % acetic acid at 25°C.

Opposite to alcohols-benzene mixtures, acetic acid in benzene suffers molecular dissociation, and the ratio of the anomalous K' (0.711) to the normal K (0.820) is 0.867, which is quite equivalent to the 0.87 calculated from Beckmann and Liesche's data above explained.

The variation of the product $K'K''$ with temperature. Substances which behave anomalous association in non-polar or polar liquids with van Arkel's association are, in most cases, hydroxylated, carboxylated, and some chlorinated compounds. Acetone-carbon bisulphide[16] is an example of the second case, and ethylene dichloride-benzene and tetrachloroethane-benzene[17] are good examples of the last case.

For one more example of hydroxylated compounds phenol-diphenylmethylamine, and for chlorinated compounds ethylene dichloride-benzene will be considered below, since the measurements done by Bramley[18] and by Faust[19] respectively on these mixtures are convenient for the consideration

Table 9. Phenol—Diphenylmethylamine (Bramley).

z_m	$\eta_{9.8°}$		$\eta_{20.1°}$	
	obs.	calc.	obs.	calc.
0.0000	0.2010	—	0.1104	—
0.0580	0.1877	0.1884	0.1048	0.1050
0.1214	0.1752	0.1755	0.0995	0.0996
0.2011	0.1614	0.1618	0.0935	0.0937
0.2803	0.1502	0.1502	0.0885	0.0885
0.3536	0.1411	0.1410	0.0845	0.0844
0.4933	0.1306	0.1286	0.0798	0.0789
0.5728	0.1226	0.1216	0.0764	0.0758
0.7106	0.1145	0.1144	0.0730	0.0729
0.8307	0.1097	0.1109	0.0715	0.0718
0.9084	0.1090	0.1098	0.0708	0.0717
1.0000	0.1096	—	0.0722	—
	$K' = 1.648$, $K'' = 1.150$. $K'K'' = 1.895$.		$K' = 1.440$, $K'' = 1.190$. $K'K'' = 1.714$.	

(15) A. E. Dunstan, *J. Chem. Soc.*, **87** (1905), 11.
(16) O. Faust, *Z. physik. Chem.*, **79** (1912), 97.
(17) W. Herz and W. Rathmann, *Z. Elektrochem.*, **19** (1913), 589.
(18) A. Bramley, *J. Chem. Soc.*, **109** (1916), 10.
(19) O. Faust, *loc. cit.*

Table 9 (*Concluded*).

x_m	$\eta_{30°}$		$\eta_{40°}$		$\eta_{60°}$		$\eta_{80°}$	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
0.0000	0.0709	—	0.0474	—	0.0253	—	0.01585	—
0.0537	0.0673	0.0676	0.0451	0.0458	0.02495	0.0250	0.01586	0.01586
0.1000	0.0650	0.0653	0.0440	0.0444	0.0247	0.0247	0.01585	0.01587
0.1557	0.0626	0.0628	0.0428	0.0431	0.02445	0.0245	0.01589	0.01590
0.2384	0.0597	0.0597	0.0415	0.0415	0.02415	0.0242	0.01594	0.01594
0.3403	0.0570	0.0567	0.0402	0.0399	0.02395	0.0239	0.01603	0.01603
0.4843	0.0542	0.0539	0.0388	0.0385	0.02375	0.0236	0.01624	0.01619
0.6720	0.0519	0.0519	0.0377	0.0377	0.0237	0.0237	0.01650	0.01649
0.8187	0.0513	0.0513	0.0376	0.0377	0.0240	0.0240	0.01682	0.01683
0.9074	0.0510	0.0512	0.03785	0.0380	0.02435	0.0244	0.01708	0.01706
1.0000	0.0513	—	0.03835	—	0.02480	—	0.01735	—

$K'=1.791$, $K''=0.812$. $K'K''=1.455$. $K'=1.557$, $K''=0.916$. $K'K''=1.585$. $K'=1.081$, $K''=1.163$. $K'K''=1.257$. $K'=0.908$, $K''=1.197$. $K'K''=1.086$.

Table 10. Benzene—Ethylene dichloride (Faust).

x_m	$\eta_{0°}$		$\eta_{34°}$		$\eta_{50°}$	
	obs.	calc.	obs.	calc.	obs.	calc.
0.0000	0.00850	—	0.00619	—	0.00418	—
0.1000	0.00843	0.00840	0.00615	0.00613	0.00422	0.00422
0.2000	0.00837	0.00837	0.00615	0.00615	0.00428	0.00428
0.3000	0.00835	0.00840	0.00620	0.00621	0.00435	0.00435
0.5000	0.00868	0.00868	0.00645	0.00645	0.00455	0.00455
0.7000	0.00933	0.00926	0.00690	0.00689	0.00492	0.00486
1.0000	0.01077	—	0.00800	—	0.00565	—

$K' = 1.132$, $K'' = 1.295$. $K'K'' = 1.466$. $K' = 0.997$, $K'' = 1.370$. $K'K'' = 1.366$. $K' = 0.721$, $K'' = 1.664$. $K'K'' = 1.200$.

of the temperature variation of the product $K'K''$. Figs. 3 and 4 show the points of the observed values lying on the calculated curves.

As seen from the footnotes of Tables 9 and 10, the decrease of the product $K'K''$ with rising temperature is a strong indication that the anomalous molecular complexity decreases with rise of temperature. This tendency expects that at sufficiently high temperature where the anomaly disappears or where they are truely chemically indifferent with each other the product $K'K''$ tends to unity.

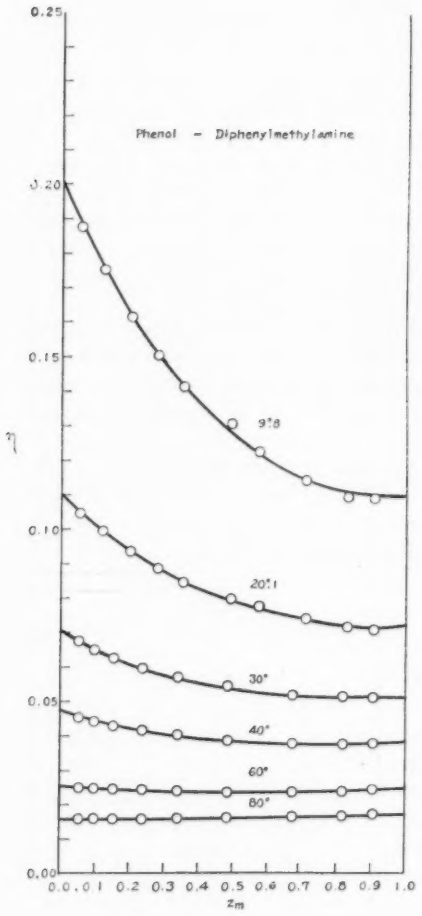

Fig. 3.

It is also noticed from these examples that the condition $K'K'' > 1$ under which anomaly of molecular complexity occurs is not always followed by a minimum in the viscosity versus concentration curves.

A further comparison of the product $K'K''$ in the formula newly proposed for liquid mixtures with the corresponding term in the Thiesen formula for gaseous mixtures. In Part II[20] we have made a little comparison of the Ishikawa formula with the Thiesen formula for gaseous mix-

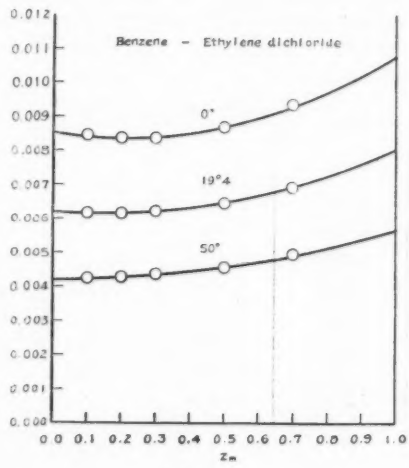

Fig. 4.

tures. The type of the Thiesen formula has been rigorously supported by the classical kinetic theory of gases,[21] the general form of which runs :

(20) T. Ishikawa, this Bulletin, **4** (1929), 5.

(21) J. P. Kuenen, "Eigenschaften der Gase," Leipzig 1919. H. Schmick, *Physik. Z.*, **29** (1928), 633.

$$\eta = \frac{\eta_1}{1+A_1\frac{z_m}{1-z_m}} + \frac{\eta_2}{1+A_2\frac{1-z_m}{z_m}},$$

$$A_1 = \left(\frac{\sigma}{S_1}\right)^2 \frac{1-\frac{m_1}{m_1+m_2}\theta_1}{0.797}\sqrt{\frac{m_1+m_2}{2m_2}}\,\frac{T+C_{12}}{T+C_1},$$

$$\theta_1 = \frac{m_1}{2(m_1+m_2)} + \frac{1}{4}\,\frac{m_1^2}{m_1^{1/2}(m_1+m_2)^{3/2}}\ln\frac{\sqrt{m_1+m_2}+\sqrt{m_2}}{\sqrt{m_1+m_2}-\sqrt{m_2}}.$$

A_2, θ_2 take the similar forms as A_1 and θ_1 respectively, in which m_1, m_2 are the molecular weights of components 1 and 2; S_1, S_2 the molecular diameters of components 1 and 2; $\sigma = \frac{1}{2}(S_1+S_2)$; C_1, C_2 the Sutherland constants of components 1 and 2; C_{12} the corresponding constant due to the attraction between a molecule of kind 1 and a molecule of kind 2; and T the absolute temperature.

Judging from the form of the formula newly proposed, one may imagine that no apparent difference is observed between these two formulae. It is of great interest, however, to note here that for gaseous mixtures whether or not the viscosity indicates a maximum the product $A_1 A_2$, the corresponding term to the product $K'K''$ in our case, is always less than or equal to unity (see Table 11), whilst for liquid mixtures $K'K''$ is always greater than or equal to unity.

Table 11.

Mixtures showing a maximum.		
Mixture	$A_1 A_2$	Observers
H_2-CH_4	0.624	Azumi, Graham, Trautz and Sorg.
$H_2-C_2H_2$	0.528	Azumi.
$H_2-C_2H_4$	0.517	Thomsen, Trautz and Stauf.
$H_2-C_2H_6$	0.508	Azumi.
$H_2-C_3H_6$	0.462	Azumi.
H_2-NH_3	0.597	Thomsen, Trautz and Heberling.
H_2-CO_2	0.404	Graham, Puluj, Thomsen, Breitenbach, Trautz and Kurz.
H_2-SO_2	0.339	Trautz and Weizel.
H_2-NO	0.467	Graham.
H_2-N_2O	0.401	Graham, Trautz and Kurz.
H_2-HCl	0.430	Trautz and Narath.
H_2-Cl_2	0.341	Thomsen.
He—Ar	0.575	Tänzler, Trautz and Kipphan, Trautz and Binkele.
He—Kr	0.454	Nasini and Rossi.
CH_4-NH_3	0.977	Jung and Schmick.
$NH_3-C_2H_4$	0.997	Thomsen, Trautz and Heberling.

Table 11 (*Concluded*).

Mixtures showing no maximum.		
Mixture	$A_1 A_2$	Observers
H_2-CO	0.491	Graham, Trautz and Baumann.
H_2-O_2	0.457	Kleint, Graham, Trantz and Melster.
H_2-N_2	0.496	Graham, Kleint, Trautz and Baumann.
H_2-Air	0.485	Graham.
H_2-He	0.806	Gille, Trautz and Kipphan, Trautz and Baumann.
H_2-Ar	0.411	Trautz and Ludewigs, Trautz and Binkele.
H_2-Ne	0.547	Trautz and Binkele.
$He-Ne$	0.739	Trautz and Kipphan.
$Ne-Ar$	0.968	Trautz and Kipphan, Trautz and Binkele.
NH_3-N_2	0.940	Thomsen, Trautz and Heberling.
NH_3-O_2	0.901	Thomsen, Trautz and Heberling.
NH_3-Air	0.973	Jung and Schmick.
NH_3-CO_2	0.901	Thomsen.
NH_3-Cl_2	0.704	Thomsen.
$Air-CO_2$	0.985	Jung and Schmick.
$Air-HCl$	0.966	Jung and Schmick.
$Air-H_2S$	0.978	Jung and Schmick.
$CO-N_2$	1.00	Trautz and Melster.
CO_2-N_2O	1.00	Trautz and Kurz.
CO_2-SO_2	0.989	Jung and Schmick.
O_2-CO_2	0.996	Graham.
$CO-O_2$	1.00	Graham, Trautz and Melster.
N_2-O_2	0.973	Graham, Kleint, Trautz and Melster.
CH_4-O_2	0.923	Graham.
$CH_4-C_2H_2$	0.983	Azumi.
$CH_4-C_2H_6$	0.967	Trautz and Sorg.
$CH_4-C_3H_8$	0.898	Trautz and Sorg.
$C_2H_2-C_3H_6$	0.985	Azumi.
$N_2-C_2H_4$	1.01	Trautz and Melster.
$CO-C_2H_4$	1.01	Trautz and Melster.
$C_2H_4-O_2$	1.06	Trautz and Melster.
C_2H_4-Air	1.00	Breitenbach.
$C_2H_6-C_3H_8$	1.01	Trautz and Sorg.
$C_3H_6-C_3H_8$	0.982	Azumi.
$C_3H_8-N_2O$	1.05	Trautz and Kurz.
$C_3H_8-CO_2$	1.04	Trautz and Kurz.

Although the formula for gaseous mixtures stands on a sound theoretical basis, a closer investigation[22] informs us that in the case where a maximum occurs the calculated viscosities are not quite coincident with the observed viscosities, giving some more or less functional divergence. On the other hand, our formula affords no such divergencies as clearly recognized from the figures above given.

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(22) H. Azumi, *Bull. Inst. Phys. Chem. Research*, **11** (1932), 1103.

ON THE FORMATION OF SYMMETRICAL DIBENZO-CYCLO-DOCOSANE-DIONE.

By **Mioji UENAKA** and **Bennosuke KUBOTA.**

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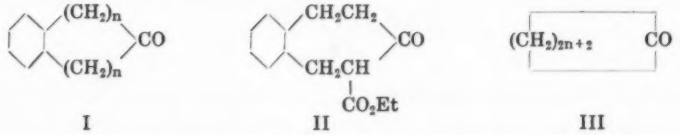
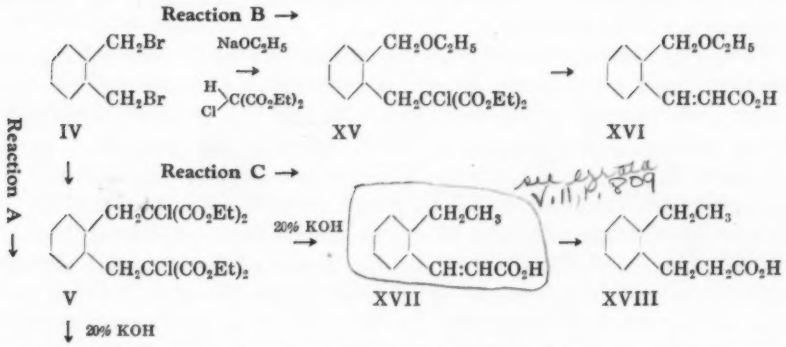
Researches designed to synthesize isocyclic ketones with a benzene ring condensed at the ortho-position have engaged our attention since the researches of Ruzicka and his collaborators[1] in the preparation of many-membered alicyclic ketones. In a previous paper[2] one of the authors described a method of synthesizing a seven-membered cyclic ketone, *o*-benzo$^{4:5}$-cycloheptanone-(1) [benzene-(pentanone-3-ylene)$_{1,2}$] (I, n = 2), which is the parent ketone of ethyl 3-ketophen-heptamethylene-2-carboxylate (II) identified by Titley[3] only as its phenylhydrazone.

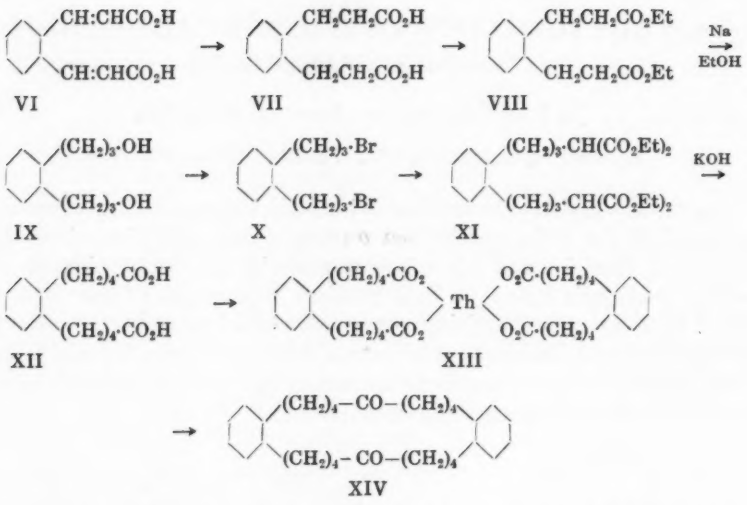


I II III

Following the compound with n = 2 in I we have further proceeded to the preparation of a series of ketones of this type intending to compare their properties with those of the alicyclic ketone III already known, and we have attempted to synthesize a compound with n = 4 in I. The course of reactions, however, resulted in the formation of a diketone XIV, symmetrical dibenzo-cyclo-docosane-dione, as shown below:



(1) Ruzicka, *Helv. Chim. Acta*, **9** (1926), 230.
(2) This Bulletin, **6** (1931), 103.
(3) Titley, *J. Chem. Soc.*, **1928**, 2571.



Starting from *o*-xylyene dibromide, *o*-phenylene-diacrylic acid was prepared by the method described by Perkin; but the reaction of *o*-xylyene dibromide with chloro-sodio-malonic ester was not so simple as we expected. When monochloro-malonic ester having a boiling point of 221–225° (corr.) was used (undoubtedly containing some dichloro-ester), the reaction, instead of taking course A, went through B and D (see experimental part), and thus resulted in the formation of *o*-(ethoxymethyl)-cinnamic acid (XVI) and phthalic alcohol diethyl-ether (XIX). This difficulty was partially overcome by preparing a monochloro-malonic ester having a boiling point 221–222°, by slightly modifying the usual method[4].

o-Phenylene-diacrylic acid (VI) was reduced to *o*-phenylene-dipropionic acid (VII) with 2% sodium amalgam. A small amount of *β*-(*o* ethylphenyl)-propionic acid (XVIII) was formed along with acid VII, when a crude acid of VI was reduced. The presence of XVIII indicates that reaction C partly took place during the hydrolysis of *o*-xylylene-dichloro-malonic ester (V) with concentrated alcoholic potash (although we have not isolated acid XVII). The scission of three molecules of carbon dioxide from *o*-xylylene-dimalonic ester (H substituted for Cl in V) by the action of concentrated alcoholic potash has already been reported by H.T. Lo[5], and the present case shows that a similar reaction also occurs to some extent in the decomposition of the dichloro-derivative of *o*-xylylene-dimalonic ester mentioned above.

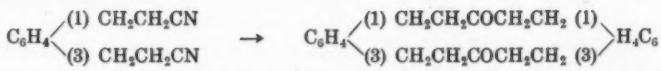
(4) Conrad, Bischoff and Guthzeit, *Ann.*, **209** (1881), 218.
(5) H. T. Lo, this Bulletin, **5** (1930), 326.

o-Phenylene-dipropionic acid diethyl ester (VIII) was reduced with sodium and alcohol to *o*-phenylene-dipropyl alcohol (IX) having a melting point 56–57°. This gave a liquid bromide (X) when treated with dry hydrogen bromide.

The condensation of malonic ester and *o*-phenylene-dipropyl bromide (X) took place readily (formation of XI), and a syrupy tetracarboxylic acid was obtained by the saponification of the ester XI; this on being heated up to 160° evolved carbon dioxide and yielded *o*-phenylene-divaleric acid (XII). The thorium salt of this acid was submitted to high vacuum dry distillation. When the distillation pressure was lower than 0.01 mm. the oily distillate partly crystallized into flat needles, which on recrystallisation gave a sharp melting point of 133.5° (corr.). The analytical results of this compound agreed with n = 4 in I, but the molecular weight determination by Rast's method (in camphor) gave a double molecular weight which corresponds to XIV: a dibenzo-cyclo-docosane-dione. The remaining part of the the distillate was redistilled and fractionated. Although the lower fraction (110–195° / 0.004 mm.) was found to yield a minute quantity of XIV after a few months, no other definite compound could be obtained by treating the liquid fractions with semicarbazide, *p*-nitrophenylhydrazine, etc.

According to the results of Ruzicka[6], and Ziegler[7] in preparing alicyclic ketones, an eleven-membered ring proved to be one of the most difficultly formed ketones, while a twenty-two-membered cyclic diketone was obtained with better result. In our case we could obtain only a twenty-two-membered cyclic diketone in a yield of about 0.2%, but could not isolate the monoketone (I, n = 4). This shows that the difficulty of the formation of an eleven-membered ring is emphasized in the case of alicyclic compounds, with a condensed aromatic ring.

A similar reaction occurring in the meta-position of benzene, first observed by Titley[8], was later confirmed by Ziegler[9] in the case of *m*-phenylene-dipropionitrile.

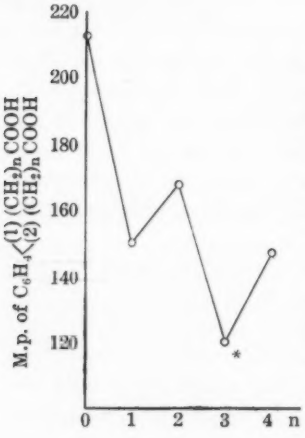


In this reaction the dinitrile, undergoing cyclisation, merely formed a diketone and practically no monoketone. The formation of such cyclic diketones as XIV in the cyclisation of *o*-$C_6H_4[(CH_2)_nCOOH]_2$ series must further be investigated.

(6) L. Ruzicka, *Helv. Chim. Acta*, **11** (1928), 672.
(7) K. Ziegler, *Ann.*, **513** (1934), 43.
(8) A. F. Titley, *J. Chem. Soc.*, **1928**, 2575.
(9) K. Ziegler, *Ann.*, **511** (1934), 6.

In regard to the odour of the diketone XIV, while the odour of the oily distillate reminds us of cedar oil, owing, perphaps, to the presence of a minute trace of the monoketone (I, n = 4), the diketone is odourless, as is the case with the alicyclic twenty-two-membered diketone obtained by Ruzicka.

Although, up to the present, we have not obtained sufficient data concerning the dicarboxylic acid series o-$C_6H_4[(CH_2)_nCOOH]_2$, there seems to exist a similar melting point rule as in the case of the aliphatic series $HOOC(CH_2)_nCOOH$, the melting point of an acid having an even number n being higher than that of the acid n−1, as can be seen in the following diagram.



Experimental.

I. Preparation of o-Phenylene-diacrylic Acid (VI). This acid was obtained by the procedure described by Perkin. For this reaction it was found necessary to use monochloro-malonic ester of good quality; otherwise o-xylylene dibromide remained unattacked, or was partly acted upon by the sodium derivative of monochloro-malonic ester, and also giving rise to the following reaction:

Reaction D o-$C_6H_4(CH_2Br)_2 + 2NaOC_2H_5 \rightarrow$
o-$C_6H_4(CH_2OC_2H_5)_2 \leftarrow o$-$C_6H_4(CH_2Br)_2 + 2KOH + 2C_2H_5OH$
XIX

The product consisted mainly of phthalic alcohol diethylether (XIX) and partly of acid XIII (described below) formed through reaction B. Therefore, in order to avoid the formation of these by-products the usual method of preparing monochloromalonic ester had to be modified.

(i) *Monochloro-malonic ester.* Dry chlorine was passed into malonic ester for a short time; the yellow solution was gently heated up to 55°, when a sudden reaction took place and hydrogen chloride was evolved. The vessel was then cooled in running water and the addition of chlorine continued until the liquid became yellow. The temperature of the ester was kept at about 30° throughout the reaction. The main part of the product boiling at 221–222° (corr.) was redistilled under reduced pressure (b.p. 116–117°/16 mm.).

(ii) *o-Xylylene dibromide* (IV). The presence of moisture during the bromination of o-xylene resulted in a considerably decreased yield of the dibromide. The crude dibromide was washed with chloroform and dried on a porous plate, m.p. 89°. This was used for the preparation of o-phenylene-diacrylic acid.

From the reagents described above, a maximum yield of 80% of o-phenylene-diacrylic acid was obtained. The crude acid was washed with alcohol, and then with benzene.

(iii) *o-(Ethoxymethyl)-cinnamic acid* (XVI). This acid was found to be formed by reaction B when monochloro-malonic ester having a higher boiling point (221–225°) was

* Observed by E. Takai. M.p. 119–120° (corr.)

used. This indicates that the presence of dichloro-malonic ester (b.p. 234°) favours reaction B. The crude product of XVI was separated from *o*-phenylene-diacrylic acid by treating the mixture with benzene (*o*-phenylene-diacrylic acid is practically insoluble in benzene). The acid XVI was then recrystallized from a mixture of acetone and water, m.p. 130-130.5° (corr.). (Found: C, 69.79; H, 7.15; mol. wt., 203 (camphor), 205 (titration). Calc. for $C_{12}H_{14}O_3$: C, 69.87; H. 6.85%; mol. wt., 206.) The presence of the ethoxyl group in the acid was proved qualitatively by the usual Zeisel method. The presence of a double bond in the side chain was confirmed by the addition of bromine (see v) and hydrogen (see vi).

(iv) *Ethyl o-(ethoxymethyl)-cinnamate.* B.p. 140-141°/2 mm. (uncorr.); n_D^{22} 1.5460. (Found: C, 71.54; H, 7.93. Calc. for $C_{14}H_{18}O_3$: C, 71.75; H, 7.75%.)

(v) *β-(o-Ethoxymethyl)-α,β-dibromopropionic acid,* C_6H_4<(1) $CH_2OC_2H_5$ / (2) $CHBrCHBrCOOH$. Acid XVI (0.2 g.) was dissolved in 10 c.c. carbon tetrachloride and 0.17 g. bromine in 5 c.c. carbon tetrachloride was added; the solution was gently heated on the water bath for a minute, when absorption of bromine took place. The solution was then left at room temperature for an hour, then washed with sodium bisulphite solution and water, and dried over sodium sulphate. After evaporating the solvent, the residue was dissolved in benzene and recrystallized by adding some petroleum ether. Colourless crystals resembling dandelion leaves separated; when heated in a capillary tube it darkened at 155° and melted into a black liquid at 168-169° (corr.). (Found: Br, 42.4. Calc. for $C_{12}H_{14}O_3Br_2$: 43.7%.)

(vi) *o-(Ethoxymethyl)-hydrocinnamic acid.* This acid was prepared by reducing acid XVI with 2% sodium amalgam. It was recrystallized from petroleum ether in colourless needles melting at 85°, and found to be soluble in water and in benzene. (Found: C, 69.38; H, 7.85. Calc. for $C_{12}H_{16}O_3$: C, 69.19; H, 7.75%.)

II. **o-Phenylene-dipropionic Acid** (VII). *o*-Phenylene-diacrylic acid (1 mol) was readily reduced by 2% sodium amalgam (6 atoms Na), and *o*-phenylene-dipropionic acid was obtained in a yield of 80-90%. When dried at 100°, a leafy sublimate was found to separate from the crude product. The sublimate, recrystallized from water, melted at 102.5°. No depression of the melting point was observed on mixing it with β-(*o*-ethylphenyl)-propionic acid prepared from *o*-xylylene-dimalonic ester[10]. This indicates that reaction C also occurs when the ester V is saponified with a 20-25% alcoholic potash.

Ethyl *o*-phenylene-dipropionate (VIII) was prepared by refluxing one part of acid with three to five parts of a 5% alcoholic solution of hydrogen chloride for three hours. The product was washed with dilute soda solution and water successively, and dried over calcium chloride; b.p. 192-193°/8 mm. (corr.) (b.p. given by Titley[11] 200-202°/12 mm.); n_D^{22} 1.4962; d_4^{22} 1.0763; MR_D obs. 75.52 (calc. 75.56).

III. **o-Phenylene-dipropyl Alcohol** (IX). Ethyl *o*-phenylene-dipropionate was reduced to this alcohol by Bouveault Blanc's method: one part of ester VIII was dissolved in seven parts of absolute alcohol and the solution was added to a flask containing one part of metallic sodium in the course of about fifteen minutes. The flask was then

(10) *Loc. cit.*, (5).

(11) Titley, *J. Chem. Soc.*, **1928**, 2578.

heated in an oil bath (120°) until the sodium was completely dissolved (A further addition of absolute alcohol was sometimes required for the complete dissolution of sodium). The solution was then slightly cooled and two parts of water added to saponify the ester which had not been reduced. It was then heated on the water bath for two hours. Ethyl alcohol was removed from the solution by steam distillation, and the residue was cooled, extracted four times with ether, washed with water, and dried over potassium carbonate. The solvent was removed and the syrupy residue was cooled to 0°. Crystallization of alcohol IX was induced by scratching the inner wall of the vessel with a glass rod, but as the alcohol crystallized with some difficulty, crystallization was effected in later runs by inoculating with the crystalline alcohol previously obtained. The product was drained on a porous plate. The yield of the crude product amounted to 30–40% of the theoretical. Increase in the yield of alcohol IX could not be attained by increasing the quantity of sodium. A considerable excess of sodium gives a rather poor yield as may be seen in the following table.

Na (atoms)/1 mol Ester VIII	8(theoret.)	12.1	12.4	16.9	18.0	23.9
Yield of Alcohol IX (%)	—	40	45	31	25	16

The alcohol was recrystallized from carbon tetrachloride. Lustrous scales, m.p. 56–57°. It is very soluble in alcohol, moderately soluble in carbon tetrachloride and difficultly soluble in ligroin. (Found: C, 73.97; H, 7.85; mol. wt., 184 (in camphor). Calc. for $C_{12}H_{18}O_2$: C, 74.17; H, 7.75%; mol. wt., 194.)

p-Xenyl-carbamate of o-phenylene-dipropyl alcohol[12], $C_6H_4[(CH_2)_3OCONHC_6H_4C_6H_5]_2$. M.p. 187°. (Found: N, 4.94. Calc. for $C_{38}H_{36}N_2O_4$: N, 4.79%.)

The ester VIII which had not been reduced, was recovered from the alkaline mother liquor as the free acid (VII) and was used in a subsequent run.

IV. **o-Phenylene-dipropyl Bromide** (X). Thirty grams of *o*-phenylene-dipropyl alcohol (IX) was heated to 130–140° in a glycerine bath and dry hydrogen bromide passed into it for five hours (three times the calculated quantity of hydrogen bromide was required). The heavy oil product was washed with dilute soda solution and then with water, dried over potassium carbonate, and distilled under reduced pressure. Yield, 35 g. B.p. 187–189°/7.5 mm. (corr.); n_D^{25} 1.5670; d_4^{25} 1.4824. (Found: Br, 50.1; MR_D, 70.13. Calc. for $C_{12}H_{16}Br_2$: Br, 50.0%; MR_D, 70.52)

V. **o-Phenylene-divaleric Acid** (XII). A sodium ethylate solution, prepared by dissolving 4.9 g. of metallic sodium in 60 g. of absolute alcohol, was slowly added to 68 g. of malonic ester. *o*-Phenylene-dipropyl bromide (X) (33.5 g.) dissolved in 100 c.c. dry ether was slowly added to the sodio-malonic ester solution. Precipitation of sodium bromide took place immediately after the addition of the bromide. After heating the mixture over a 50-watt carbon lamp for three hours, the excess of malonic ester was removed by distilling it under reduced pressure, and the residue was saponified by heating with 20% alcoholic potash (45 g. potassium hydroxide) on the water bath for six hours. The alcohol

(12) The authors wish to thank Mr. T. Akita for preparing and identifying this compound.

was then driven off and the reside was dissolved in some water and the oily matter insoluble in the alkaline solution was removed by shaking with ether. *o*-Phenylene-dipropyl malonic acid separated as a syrupy mass on neutralizing the solution with dilute hydrochloric acid. The viscous acid was dissolved in ether and dried over anhydrous sodium sulphate; after removal of the ether, the syrupy residue was heated to 120-160°, when it decomposed into *o*-phenylene-divaleric acid (XII) and carbon dioxide. A part of the crude product was purified by dissolving it in a dilute sodium carbonate solution and heating on the water bath for an hour with the addition of animal charcoal. The acid thus obtained was recrystallized from a mixture of acetone and water. Colourless crystals, m.p. 148-149° (corr.). The yield was 90% of the theoretical. (Found: C, 68.98; H, 8.34; mol. wt., 285 (in camphor), 280 (titration, as dibasic acid). Calc. for $C_{16}H_{22}O_4$: C, 69.02; H, 7.97%, mol. wt., 278.) It is soluble in acetic acid, alcohol, chloroform, and acetic ester, difficultly soluble in cold water, and insoluble in petroleum ether.

VI. **The Symmetrical Dibenzo-cyclo-docosane-dione (XIV).** Twenty grams of *o*-phenylene-divaleric acid was dissolved in 1 l. of water by neutralizing it with sodium carbonate. Fourteen grams of thorium chloride, dissolved in 400 c.c. of water, was slowly added to the former solution with constant mechanical stirring. The yield of the thorium salt was 29.4 g. This was divided into two portions and each portion placed in a 30 c.c. distilling flask provided with a large side tube. The salt was subjected to high vacuum dry distillation by heating the flask in salt bath ($LiNO_3$-$NaNO_3$-KNO_3) of 160° and then gradually raising the temperature to about 400° in the course of eight to ten hours, the pressure meanwhile being 0.008-0.009 mm. A light yellow, viscous substance distilled over from 190° (bath temperature), a part of it solidifying into long needles after four to six hours from the beginning of distillation. The total yield of the distillate was 2.4 g. This was placed in an ice box for a few days, and the crystals were then separated. The solid product is soluble in ordinary organic solvents. It was recrystallized from ligroin with great ease. Yield, 25 m.g., m.p 133.5° (corr.). In a third run, when 6.7 g. of the salt was used, the yield of the solid product was 4.5 mg. In this case the distillation was carried out under a comparatively high pressure, i.e., 0.01-0.1 mm., and the product was found to give small oblong plates only after a few weeks' cooling in an ice box. These crystals, when recrystallized from ligroin by inoculating with the flat needles previously obtained, were changed into needle-like crystals identical with those obtained in the first distillation. (Found: C, 83.18; H, 9.43; mol. wt., 430, 439 (in camphor). Calc. for $C_{30}H_{40}O_2$: C, 83.27; H, 9.39%; mol. wt. 432.)

The semicarbazone was prepared in the usual way by adding semicarbazide acetate to the ketone (XIV) and adding alcohol until solution was complete. The reaction mixture was allowed to stand overnight at room temperature when a flocculent mass separated. The alcoholic solution was diluted with water and the flocculent precipitate was collected. As the product was difficultly soluble in absolute alcohol and practically insoluble in other solvents, it was successively washed with hot water, alcohol, ligroin, and dried in vacuum. Decomp. pt. 205-208° (corr.) (turns red). (Found: N, 14.8, 13.6. Calc. for $C_{32}H_{46}O_2N_6$: N, 15.4%). Yellow microscopic needles, probably the *p*-nitrophenylhydrazone were obtained by treating XIV with *p*-nitrophenylhydrazine; m.p. 168-172°. The substance was so scarce that analysis was impossible.

The remaining liquid part of the distillate was treated with semicarbazide, *p*-nitrophenylhydrazine, etc., but no definite product could be obtained. It was therefore redistilled and the two following fractions were collected: (1) 110-195/0.004 mm., (2)

195–250 / 0.004 mm. On standing for five months, 0.8 mg. of ketone XIV was found to have crystallized from fraction (1); no change was observed in fraction (2). Both fractions were treated with semicarbazide etc., but no derivative could be obtained. The analytical results of the fractions were: (1) C, 86.22; H, 9.51; (2) C, 87.07; H, 9.47%.

Summary.

The synthesis of an eleven-membered carbon ring attached to the ortho-position of benzene was attempted. The dry distillation of the thorium salt of *o*-phenylene-divaleric acid resulted in the formation of a twenty-two-membered diketone ring. Several new compounds incidental to the synthesis are reported.

In concluding, the authors wish to thank Mr. S. Tsutsumi and Mr. H. Yamura for the valuable assistance given us.

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DECENOIC ACID $C_{10}H_{18}O_2$ IN SPERM HEAD OIL.*

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Whilst in preceding papers[1] the separation of denticetic acid ($\Delta^{5:6}$-dodecenoic acid) from sperm blubber and head oils was described, the present paper deals with the separation of a decenoic acid—a lower homologue of denticetic acid—from sperm head oil. The only one decenoic acid in natural fats recorded in the literature is $\Delta^{9:10}$-decenoic acid discovered by Grün and Wirth[2] as an extremely minor constituent of butter fat; the presence of decenoic acid in sperm head oil has so far never been known before the present experiment.

In a previous experiment[3] of the separation of hexadecenol and tetradecenol in the unsaponifiable matter of sperm head oil, the liquid oil obtained by removing the crystalline solid was first subjected to the methanolysis, and

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* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1313.

(1) This Bulletin, **10** (1935), 563, 570.

(2) *Ber.*, **55** (1922), 2197.

(3) This Bulletin, **10** (1935), 573.

the resulting mixture of methyl esters and free unsaponifiable matter was fractionated, by which a fraction boiling below 180°/15 mm. was separately collected. This fraction was saponified, and the fatty acids and the unsaponifiable matter were separated in the usual way.

Whilst the unsaponifiable matter was worked up further in the previous experiment, the fatty acids obtained above were used in the present experiment. They were fractionated, and a fatty acid fraction boiling below 160°/15 mm. was separated. For the separation of unsaturated acids, this fraction was treated by the bromo-ester distillation method of Grün and Janko.[4] In this method the fatty acid fraction was converted into the methyl esters, and then brominated in ethereal solution. The product was distilled under reduced pressure, by which the saturated methyl esters were removed as distillate. The residue containing the bromides derived from the unsaturated methyl esters was debrominated, and the product was saponified to regenerate the unsaturated acids, which were then fractionated to yield decenoic acid.

The decenoic acid thus obtained was converted into the methyl ester, and the latter was oxidised with potassium permanganate in acetone. After the oxidation products were saponified to liberate the free acid from the acid ester, azelaic acid $HOOC{\cdot}(CH_2)_7{\cdot}COOH$ was identified, and formic acid $H{\cdot}COOH$ was also detected. Accordingly the constitution of decenoic acid is to be represented by the formula $CH_2{=}CH{\cdot}(CH_2)_7{\cdot}COOH$. It is thus seen that decenoic acid in sperm head oil is identical with $\Delta^{9:10}$-decenoic acid which was found by Grün and Wirth in butter fat.[5]

Experimental.

1. **Separation of Decenoic Acid.** In a previous experiment[3] of the separation of hexadecenol and tetradecenol, the sperm head oil having saponification value 147.7, iodine value (Wijs) 53.4 and unsaponifiable matter 36.52% was first pressed to remove the solid portion, and the liquid portion obtained in a yield of about 80% was subjected to the methanolysis. The product (10 kg) consisting of the methyl esters and the free unsaponifiable matter was fractionated, and a fraction boiling below 180°/15 mm. was separately collected. This fraction was saponified, the resulting soap solution was extracted with

(4) *Z. Deuts. Oel-u. Fett-Ind.*, **41** (1921), 553, 572.

(5) Grün stated that he and his co-workers found dodecenoic ($\Delta^{11:12}$-?) and tetradecenoic ($\Delta^{13:14}$-?) acids besides $\Delta^{9:10}$-decenoic acid in butter fat (*Z. angew. Chem.*, **37** (1924), 228). It should be noted that whilst decenoic acid in sperm head oil is found to be identical with that in butter fat, dodecenoic and tetradecenoic acids in sperm head oil were confirmed to be $\Delta^{5:6}$-dodecenoic (denticetic) and $\Delta^{5:6}$-tetradecenoic (physeteric) acids, respectively; neither $\Delta^{11:12}$-dodecenoic nor $\Delta^{13:14}$-tetradecenoic acid was found in sperm head oil.

ether, and the fatty acids and the unsaponifiable matter were separated in the usual way. Whilst the unsaponifiable matter was used for the isolation of hexadecenol and tetradecenol, the fatty acids were used for the present experiment. These were fractionated, and there was obtained 282 g. of a fraction boiling below 180°/15 mm. and having neutralisation value 301.9 and iodine value 26.2. This fatty acid fraction was refractionated, giving 61 g. of a fraction which distilled below 160°/15 mm. and had neutralisation value 338.2 and iodine value 18.3. This was converted into methyl esters, and the latter were brominated in ethereal solution under cooling with ice. After the ethereal solution had been freed from the excess of bromine by washing with sodium thiosulphate solution, it was washed with water and then dehydrated over anhydrous sodium sulphate. On distilling off the solvent from the ethereal solution, the product of bromination was distilled under 5 mm. When the distillation was continued up to 120°/5 mm., the rate of the distillation of saturated esters became very slow, and the operation was stopped. The residue containing the bromides derived from unsaturated esters was debrominated with zinc powder and sulphuric acid in methanol solution, and the product was saponified, yielding 9 g. of unsaturated acids. These were subjected to a further fractionation, by which the distillation began at 141°/15 mm., and 1.5 g. of a fraction boiling at 143–148°/15 mm. was separately collected as decenoic acid $C_{10}H_{18}O_2$ (Found: C, 70.47; H, 10.70. Calc. for $C_{10}H_{18}O_2$: C, 70.53; H, 10.66%). It had the following constants: d_4^{15} 0.9238, d_4^{20} 0.9203, n_D^{15} 1.4507, n_D^{20} 1.4488, molecular refraction (based on the data at 15°) 49.56 (calc. for $C_{10}H_{18}O_2$ F_1: 49.45), neutralisation value 328.3 (calc. 329.7), iodine value 134.0 (calc. 149.2).

Hydrogenation of the decenoic acid yielded capric acid $C_{10}H_{20}O_2$ which, after being recrystallised from 70% alcohol, showed neutralisation value 325.1 (calc. 325.9), m.p. 30–30.5° and mixed m.p. 30.5–31°.(6) Unlike other mono-ethylenic acids, the decenoic acid yielded no crystalline dihydroxy derivative by oxidation with a dilute alkaline solution of potassium permanganate.

2. **Oxidation of Methyl Decenoate.** The decenoic acid obtained above was converted into the methyl ester by means of hydrogen chloride in methanol solution. The methyl ester (1.0 g.) was dissolved in 10 c.c. of acetone, and 4 g. of finely powdered potassium permanganate was added in small portions. After heating for 4 hours on the water-bath under reflux condenser the acetone was removed by distillation, and 30 c.c. of water was added to the residue. A current of sulphur dioxide was passed into the mixture until the excess of potassium permanganate and the insoluble oxides of manganese disappeared completely. The oxidation products were extracted with 300 c.c. of ether, and the ethereal solution was treated with potassium carbonate solution in order to dissolve out the acidic oxidation products as their potassium salts. The aqueous solution containing the potassium salts was heated on the water-bath with the addition of a little potassium hydroxide to saponify the acid ester. On decomposing the potassium salts with hydrochloric acid, the acidic substances liberated were taken up with ether. The ethereal solution was washed with brine, and ether was removed by distillation. The residue consisted mainly of a crystalline solid having a strong penetrating odour; yield 0.7 g. It was treated with petroleum ether, and the petroleum ether solution was separated from the insoluble portion. On distilling off the solvent from the petroleum ether solution, there was obtained a small amount of residue which had a smell of

(6) The specimen of capric acid used for the mixed melting point test was separated from the seed oil of *Cinnamomum pedunculatum*; m.p. 30.5–31°.

formic acid and was soluble in water. The distillate of petroleum ether had also a smell of formic acid. On warming the aqueous solution of the residue with solutions of silver nitrate, metallic silver was deposited. When reduced with hydrochloric acid and metallic magnesium, the aqueous solution gave a smell of formaldehyde, the presence of which was confirmed by the violet colouration when the mixture of this solution, fresh milk and hydrochloric acid containing a trace of ferric chloride were heated gently.

The portion insoluble in petroleum ether yielded azelaic acid $C_9H_{16}O_4$ on recrystallisation from benzene; neutralisation value 594.2 (calc. 596.5), m.p. and mixed m.p. 105–106°[7] (Found: C, 57.28; H, 8.69. Calc. for $C_9H_{16}O_4$: C, 57.41; H, 8.57%).

Summary.

A decenoic acid has been separated from sperm head oil. Its methyl ester was oxidised with potassium permanganate in acetone, and after the saponification of the acid ester contained in the oxidation products, azelaic acid was identified. The presence of formic acid in the oxidation products was also indicated. Accordingly the decenoic acid in sperm head oil is proved to be $\Delta^{9:10}$-decenoic acid, having the formula $CH_2{=}CH{\cdot}(CH_2)_7{\cdot}COOH$.

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THE HIGHLY UNSATURATED ALCOHOLS IN SPERM BLUBBER OIL.*

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In a former study on the unsaponifiable matter of sperm blubber oil, one of the authors[1] separated and identified oleyl alcohol as the chief constituent together with such substances as cetyl alcohol, octadecanol and cholesterol, but other unsaponifiable constituents present in a minor proportion were not closely examined. Later, we[2] have attempted to separate and investigate these minor constituents, and recently described the results of our experi-

7) The specimen of azelaic acid used for the mixed melting point test was prepared by the ozonolysis of oleic acid; m.p. 105–106°.

* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1316.

(1) Toyama, *J. Soc. Chem. Ind., Japan*, **30** (1927), 527.

(2) This Bulletin, **10** (1935), 579.

ments in which zoomaryl alcohol ($\Delta^{9:10}$-hexadecenol) was separated and its constitution was established. The present paper deals with the highly unsaturated alcohols which are present as minor constituents in the unsaponifiable matter of this oil. A review of the literature shows that the following facts have hitherto been reported in connection with the highly unsaturated alcohols in sperm oil. One of the authors, in his previous study on the unsaponifiable matter of sperm blubber oil, indicated the presence of some highly unsaturated alcohols by the fact that bromination of a fraction of the unsaponifiable matter of this oil yielded a small amount of ether insoluble bromides and also petroleum ether insoluble bromides having high Br-contents. Also Hilditch and Lovern[3] stated the presence of some highly unsaturated alcohols (mainly di-ethylenic) among C_{18}- and C_{20}-unsaturated alcohols in sperm blubber oil. According to André and François[4] the liquid fraction of the unsaponifiable matter of sperm oil contains, in addition to oleyl alcohol, alcohols of higher molecular weight and higher unsaturation than oleyl alcohol, and yields a petroleum ether insoluble bromide having the formula $C_{22}H_{42}OBr_4$. It is thus seen that, although the presence of some highly unsaturated alcohols has already been pointed out by several authors, our knowledge of the individual constituents of these highly unsaturated alcohols has hitherto been scanty.

In the previous experiment of the separation of zoomaryl alcohol in sperm blubber oil, the unsaponifiable matter of this oil was separated into 5 fractions by fractional distillation, and the lowest fraction boiling below 188°/5 mm. was worked up further for the isolation of zoomaryl alcohol. Since the highly unsaturated alcohols originally present in the unsaponifiable matter in a small proportion were deemed to have been concentrated in the highest fraction, the latter was used for the present experiment. A small amount of solid saturated alcohols was removed from this fraction, and the liquid alcohols were brominated. The ether insoluble bromides were separated and then debrominated to regenerate the highly unsaturated alcohols. These were then converted into acetates, and the latter were separated into 12 fractions by fractional distillation. The 3rd fraction had saponification and iodine values which agreed with those calculated for the acetate ($C_{22}H_{36}O_2$) of a highly unsaturated alcohol $C_{20}H_{34}O$. The free alcohol obtained on saponification of this fraction showed an elementary composition which corresponded to the formula $C_{20}H_{34}O$, and yielded on bromination an ether insoluble bromide of the formula $C_{20}H_{34}OBr_8$. The 1st and 2nd fractions showed saponification values which were a little higher than the value calculated for $C_{22}H_{36}O_2$, and

(3) *J. Soc. Chem. Ind.*, **48** (1929), 365 T.
(4) *Compt. rend.*, **185** (1927), 279.

consequently these fractions were thought to contain, in addition to the acetate of $C_{20}H_{34}O$, the acetates of some highly unsaturated alcohols of lower molecular weight (possibly the acetates of $C_{18}H_{32}O$ and $C_{18}H_{30}O$). A saturated alcohol $C_{20}H_{42}O$ was separated from the hydrogenation product of the free alcohols from the 1st–3rd fractions, and it was oxidised with chromic acid, yielding arachidic acid $C_{20}H_{40}O_2$. Accordingly the highly unsaturated alcohol $C_{20}H_{34}O$, which is present as its acetate in these fractions, is a primary alcohol having no branched chain of carbon atoms. The 12th fraction showed a saponification value which was a little higher than that calculated for the acetate ($C_{24}H_{38}O_2$) of an alcohol $C_{22}H_{36}O$, but the iodine value of this fraction agreed with the value calculated for $C_{24}H_{38}O_2$. The free alcohol yielded an ether insoluble bromide having the formula $C_{22}H_{36}OBr_{10}$. Hence the alcohol, which was present as its acetate in the 12th fraction, was deemed to consist mainly of $C_{22}H_{36}O$. The fact that the saponification value of the 12th fraction was higher than the value calculated for $C_{24}H_{38}O_2$ is presumably ascribed to the contamination of the acetates of some polyvalent alcohols (possibly some highly unsaturated alcohols belonging to the selachyl alcohol group). A further investigation is yet wanted to confirm these postulations. The hydrogenation product of the free alcohol yielded, after repeated recrystallisation, a saturated alcohol which showed an acetyl value corresponding to $C_{22}H_{46}O$.

It is thus seen from the results of the present experiment that the highly unsaturated alcohols in the unsaponifiable matter of sperm blubber oil contain two alcohols $C_{20}H_{34}O$ and $C_{22}H_{36}O$ as chief constituents. These two alcohols have the formula just corresponding to eicosatetraenoic acid $C_{20}H_{32}O_2$ and clupanodonic acid $C_{22}H_{34}O_2$ which occur in sperm blubber and other marine animal oils as chief constituents of highly unsaturated acids. Although no individual constituents of highly unsaturated alcohols other than $C_{20}H_{34}O$ and $C_{22}H_{36}O$ have been found with certainty in the present experiment, it is very probable that a further investigation, starting with a large quantity of material, may bring out a sufficient evidence for the presence of several individual constituents of highly unsaturated alcohols corresponding to those of highly unsaturated acids in marine animal oils. Postulating from the relations of the constitutions of physeteryl and zoomaryl alcohols[5] and the corresponding fatty acids in marine animal oils, two highly unsaturated alcohols $C_{20}H_{34}O$ and $C_{22}H_{36}O$ in sperm blubber oil may have ethylenic linkings in the same positions as eicosatetraenoic[6] and clupanodonic acids,[7] i.e., these

(5) Toyama and Tsuchiya, this Bulletin, **10** (1935), 573; Toyama and Akiyama, this Bulletin, **10** (1935), 579.

(6) Toyama and Tsuchiya, this Bulletin, **10** (1935), 296.

(7) Toyama and Tsuchiya, this Bulletin, **10** (1935), 441.

alcohols may possibly be identified as the alcohols obtained on reducing the carboxyl group of the corresponding highly unsaturated acids. We are intended to confirm this by subsequent experiments. Whilst the alcohol $C_{20}H_{34}O$ (eicosatetraenol), for which we propose the name catadonyl alcohol,[8] has never been recorded in the literature, the docosapentenol (clupanodonyl alcohol) $C_{22}H_{36}O$ was prepared by Tsujimoto and Kimura[9] by the reduction of methyl clupanodonate, but its occurrence in natural oils has never been reported before our experiment.

Experimental.

1. **The Preparation of Ether Insoluble Bromides from High Boiling Fraction and the Regeneration of Highly Unsaturated Alcohols by Debromination.** A specimen of sperm blubber oil having saponification value 126.8, iodine value (Wijs) 82.6 and unsaponifiable matter 38.98% was heated with barium hydroxide solution under pressure, and a mixture of barium soaps and free unsaponifiable matter was obtained, from which the latter was extracted with acetone. The unsaponifiable matter was separated into 5 fractions by fractional distillation, the yield of the highest fraction boiling at 195–198°/5 mm. being 1,680 g. from 10,070 g. of unsaponifiable matter. For the details of the above experiment the previous paper[3] should be consulted.

The highest fraction obtained above showed acetyl value 182.6 and iodine value 96.8. This fraction (1,670 g.) was divided into three batches, and each of them was dissolved in about 10 times its quantity of acetone. The solution was cooled down to about -10°, the separated solid (yield 70 g. in total, iodine value 14.5) was filtered, and on distilling off the solvent from the filtrate there was obtained the liquid portion having iodine value 100.9. The liquid portion (1,570 g. in total) was brominated in the following manner: this was divided into 3 batches consisting of 520–530 g., and each of them was dissolved in about 10 times its quantity of ether. The solution was cooled down to about -10°, and an excess of bromine (about 400 g.) was added in the course of 5 hours under constant stirring. After the completion of the addition of bromine, the solution was allowed to stand in the cold for 2 hours more and then the precipitate of insoluble bromides (53.5 g. in total) was filtered and washed with cold ether until the precipitate became white. The filtrate together with the washings was washed with sodium thiosulphate solution to remove the excess of bromine, and after subsequent washing with water and dehydration over anhydrous sodium sulphate, the solvent was distilled. The residue was then dissolved in about 10 times its quantity of petroleum ether, the solution was cooled down to about -10°, and the precipitated bromides (35 g. in total) were filtered off. The ether insoluble bromides had Br-content 69.50% and melted to a tar-like matter at about 240°. The petroleum ether insoluble bromides had Br-content 64.40% and turned black at about 150°. Fifty-three g. of ether insoluble bromides were mixed with 27 g. of zinc powder, and 80 c.c. of ethyl alcohol was added to the mixture. The liquid was heated on the water-bath under a reflux condenser, and 80 c.c. of 5 N hydrochloric acid in ethyl alcohol was added in the course of 1.5 hours. After heating 1 hour more, the supernatant solution was decanted off. The residue was again treated with 27 g. of zinc powder, 80 c.c. of ethyl alcohol and 80 c.c. of 5 N hydrochloric acid in

(8) Derived from Catadontidae.
(9) *J. Soc. Chem. Ind., Japan*, **28** (1925), 390.

ethyl alcohol as before, and then the solution was separated from the insoluble substances which were thoroughly washed with ethyl alcohol. The united solutions and the washings were diluted with a large quantity of water, and the debrominated product, which separated as an oily layer, was collected by using ether. The highly unsaturated alcohols (15.3 g.) thus obtained by debromination of ether insoluble bromides had acetyl value 166.7, iodine value 383.9[10] and n_D^{20} 1.4926. They showed a drying power and had a peculiar smell like the highly unsaturated acids in marine animal oils. A portion of the highly unsaturated alcohols was subjected to hydrogenation, and the product was recrystallised from 90% ethyl alcohol, yielding the recrystallised product and the portion recovered from the mother liquor (Table 1). The latter was, however, suspected to contain more or less unsaturated alcohols which escaped a complete hydrogenation. The acetyl values (saponification values of the corresponding acetates) calculated for $C_{18}H_{38}O$, $C_{20}H_{42}O$, and $C_{22}H_{46}O$ are shown in Table 2.

Table 1.

	M.p.	Acetyl value
Recrystallised product	64°	156.8
Portion recovered from the mother liquor	57°	171.5

Table 2.

	$C_{18}H_{38}O$	$C_{20}H_{42}O$	$C_{22}H_{46}O$
Acetyl value	179.6	164.9	152.3

2. **Fractionation of Highly Unsaturated Acetates.** The highly unsaturated alcohols were heated with acetic anhydride, and 15.8 g. of the resulting acetates were fractionally distilled with the results shown in Table 3.

Table 3.

Fraction	B.p. (°C./5 mm.)	Saponif. value	Iodine value	n_D^{20}	Yield (g.)
1	185-202	173.2	296.4	1.4798	0.8
2	202-207	171.6	303.0	1.4800	1.0
3	207-211	169.1	308.3	1.4804	1.3
4	211-213	168.3	309.9	1.4808	1.0
5	213-215	168.1	310.8	1.4809	1.2
6	215-217	167.9	312.0	1.4810	1.2
7	217-218	167.5	313.6	1.4817	1.3
8	218-219	166.1	315.9	1.4828	1.7
9	219-220	165.8	318.1	1.4835	1.4
10	220-221	164.2	325.5	1.4839	1.5
11	221	163.7	333.0	1.4843	1.3
12	221-225	165.1	349.9	1.4868	1.5
Residue and loss	—	—	—	—	0.6

The saponification and iodine values of the fraction (3) are close to the corresponding values (saponification value 168.8, iodine value 305.6) for the acetate $C_{22}H_{36}O_2$ of a highly unsaturated alcohol $C_{20}H_{34}O$. The free alcohol obtained on saponification of this fraction was found to have the formula $C_{20}H_{34}O$ by elementary analysis (Found: C, 82.31;

(10) This value is thought to be a little too high.

H, 11.89. Calc. for $C_{20}H_{40}O$: C, 82.68; H, 11.80%).[11] The hydrogenated product of the free alcohol showed acetyl value 164.4 (calc. for $C_{20}H_{42}O$: 164.9) and m.p. 62.5–63° after recrystallisation from 90% ethyl alcohol (Found: C, 80.19; H, 14.20. Calc. for $C_{20}H_{42}O$: C, 80.45; H, 14.19%). The melting point of *n*-eicosanol is recorded as 65–65.5°.[12] On brominating the free alcohol in ethereal solution, there was obtained 56% of an ether insoluble bromide which showed Br-content 68.82% (calc. for $C_{20}H_{34}OBr_8$: 68.77%) and turned black at about 240°.

The saponification values of the fractions (1) and (2) are a little higher than the value calculated for the acetate $C_{22}H_{36}O_2$ of an alcohol $C_{20}H_{34}O$, but on hydrogenating the free alcohol liberated from the fractions (1) and (2), there was obtained the same product having acetyl value 164.3 and m.p. 62.5–63° as that described in the case of the fraction (3).

The saturated alcohol (0.8 g.) described above, m.p. 62.5–63°, was dissolved in 30 c.c. of glacial acetic acid, and 3.5 g. of chromic acid was added. The solution was heated on the water-bath under a reflux condenser for 2 hours. On cooling it was diluted with water, and the oxidation products were extracted with 500 c.c. of ether. The ethereal solution was washed with water and then with potassium hydroxide solution by which the acidic oxidation products were converted into the potassium salts and separated from the ethereal solution. The aqueous solution containing the potassium salts was decomposed with hydrochloric acid, and the insoluble acidic substances were separated and recrystallised from 95% ethyl alcohol. The product showed neutralisation value 181.5 (calc. for $C_{20}H_{40}O_2$: 179.6) and m.p. 73.5–74°. No depression of melting point was observed when the product was admixed with a pure specimen of arachidic acid $C_{20}H_{40}O_2$ (m.p. 74.5–75°).

The highest fraction (12) showed a saponification value which is considerably higher than the value calculated for the acetate $C_{24}H_{38}O_2$ of a highly unsaturated alcohol $C_{22}H_{36}O$, but the free alcohol obtained on saponification of this fraction showed an elementary composition corresponding to the formula $C_{22}H_{36}O$ (Found: C, 83.28; H, 11.38. Calc. for $C_{22}H_{36}O$: C, 83.47; H, 11.47%). On brominating the free alcohol in ethereal solution, there was obtained 57% of an ether insoluble bromide which had Br-content 71.45% (calc. for $C_{22}H_{36}OBr_{10}$: 71.65%) and turned black at about 240°. The hydrogenation product showed acetyl value 152.2 (calc. for $C_{22}H_{46}O$: 152.3) and m.p. 67–67.5° after repeated recrystallisation from 90% ethyl alcohol. The melting point of *n*-docosanol $C_{22}H_{46}O$ is recorded as 70–70.5°.[13]

Summary.

The high boiling fraction of the unsaponifiable matter of sperm blubber oil was brominated in ethereal solution, and the ether insoluble bromide was separated and then debrominated to regenerate the highly unsaturated alcohols. These were converted into acetates, and the latter were fractionated. An examination of the resulting fractions showed that the highly unsaturated alcohols of sperm blubber oil contained two individual alcohols $C_{20}H_{34}O$ and $C_{22}H_{36}O$ as chief components.

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(11) For the elementary analyses we are indebted to Mr. Tsuchiya.
(12) Adam and Dyer, *J. Chem. Soc.*, **127** (1925), 70.
(13) Bleyberg and Ulrich, *Ber.*, **64** (1931), 2504.

GEWINNUNG DER FESTEN FIBER AUS REISSTROH.

Von Munenari TANAKA.

Eingegangen am 27. November 1935. Ausgegeben am 28. Januar 1936.

Es gibt wenig Arbeiten über die Isolierung der α-Zellulose aus Reisstroh. Früher glaubte man, es gäbe überhaupt keine röhrenförmige Zellulose im Stroh. Diesmal ist es nun dem Verfasser nach fünfjähriger Forschung gelungen, röhrenförmige Zellulose im Stroh zu isolieren.

Zur Isolierung wird zuerst die Zellulose mit "Nibe"[1] (*Hydrangea paniculata* Sieb.) verstärkt, und dann mit Myrrhe[2] oder Weihrauch[3] zusammengebracht wie bei der Färbungsmethode der Zellulose mit Küpenfarbstoff. Diese Zellulose lässt man endlich mit Ammoniumcarbonat und Natriumbicarbonat schwellen. Zu diesem Zwecke wurden die Blattscheiden anstatt der Halme benutzt, da die ersteren viel mehr Zellulose als die letzteren enthalten.

Beispiel: 100 g. Stroh werden mit 70 g. Ätznatron in 15 Liter Wasser erhitzt und nach 40 Min. wird das Produkt mit Wasser gewaschen. Die Zellulose wird darauf mit 7 g. "Nibe" und 1/2 Liter Wasser etwa 15 Min. unter Zufügung von wenig Natriumperoxyd aufgekocht und gut gewaschen. Dann werden zur Zellulose 800 c.c. heisses Wasser 7 g. Myrrhe (5% ig verdünnt mit Natriumbicarbonat), 0.1 g. Brankit hinzugefügt, und ein paar Minuten stehen gelassen. Dazu kommen 1.5 g. Oxalsäure und 6 g. Chlorkalk und endlich erhält man bei der Zugabe der Mischung von 5 g. Natriumbicarbonat und Ammoniumcarbonat bei 50° feste Fiber. Die Ausbeute beträgt 20% des Ausgangsmaterials. Die Analyse dieses Produkts ist folgende: (1) Wassergehalt 7.15%; (2) Elementaranalyse: (A) Subst., 5.612 mg.; Asche, 0.013 mg.; C, 45.7%; H, 6.7%; (B) Subst., 5.086 mg.; Asche, 0.045 mg.; C, 46.2%; H, 6.9%.

Diese feste Fiber ist etwas stärker als Naturwatte. Der Unterschied zwischen dem künstlichen und dem Naturprodukt besteht darin, dass das künstliche nicht gedreht ist.

Kobe College.

(1) Wiesner, „Die Rohstoffe der Pflanze," Bd. II, 391.
(2) Köhler, „Medizinal Pflanzen," Bd. I, 303-306.
(3) *Ibid.*, Bd. I, 299.

ÜBER DEN UNTERSCHIED IN DER ISOTOPENZUSAMMENSETZUNG VON LUFT- UND WASSERSAUERSTOFF.

(Vorläufige Mitteilung.)

Von Noriyoshi MORITA und Toshizo TITANI.

Eingegangen am 3. Dezember 1935. Ausgegeben am 28. Januar 1936.

Beim Vergleich von zahlreichen Versuchen über den Deuterium-Gehalt von gewöhnlichem Wasser sowie die elektrolytische Trennung von Sauerstoffisotopen, kam uns die Vermutung, dass der Sauerstoff in der Luft, den wir Luftsauerstoff nennen wollen, spezifisch schwerer sei als der Wassersauerstoff, der im Wasser mit Wasserstoff gebunden ist. Um diese Vermutung näher zu prüfen haben wir ein Experiment durchgeführt, dessen Ergebnisse wir vorläufig mitteilen wollen.

Zunächst wurde leichtes oder Deuterium-armes Wasser durch die fraktionierte Elektrolyse von gewöhnlichem Wasser hergestellt. Durch nochmalige Elektrolyse dieses leichten Wassers konnten wir den leichten Wasserstoff, dessen D-Gehalt schätzungsweise kleiner als 1 Atom in 30,000 war, sich entwickeln lassen. Den so erhaltenen leichten Wasserstoff haben wir separat mit dem Luft- und Wassersauerstoff zu Wasser rekombiniert und die Dichten des jeweils entstehenden Wassers miteinander verglichen. Dazu verwendeten wir die folgenden drei Sorten von Sauerstoff: Sauerstoff (I) war Luftsauerstoff. In der Praxis verwendeten wir die atmosphärische Luft, die im voraus gut gereinigt und getrocknet war. Sauerstoff (II) war Wassersauerstoff, der durch teilweise Elektrolyse aus gewöhnlichem Wasser gewonnen wurde. In diesem Sauerstoff (II) kann man die extreme Verschiebung der Isotopenzusammensetzung inolge der elektrolytischen Trennung erwarten, weil nur 5% vom gesamten Elektrolysierwasser gespalten worden war. Sauerstoff (III) war ebenfalls durch die Elektrolyse erhaltener Wassersauerstoff. Aber in diesem Fall wurde die Elektrolyse fast bis zum Ende durchgeführt, d.h. 95% vom totalen Volumen elektrolytisch gespalten. Infolgedessen muss Sauerstoff (III) dieselbe Isotopenzusammensetzung wie der Sauerstoff, der im Wasser chemisch verbunden ist, besitzen.

Die Rekombination von so hergestelltem Sauerstoff mit dem leichten Wasserstoff führten wir über dem auf 300° bis 350°C. erhitzten Kupferkatalysator durch, der aus Kupferoxyd durch die Reduktion mittels Wasserstoffs hergestellt worden war. Wir verwendeten immer den Wasserstoff in grossem Überschuss, um den Sauerstoff vollständig reagieren zu lassen.

Dabei funktionierte der Kupferkatalysator auch als ein sehr effektives Reservoir für den Sauerstoff. Nach dem Experiment wurde der leichte Wasserstoff noch lange Zeit über den erhitzten Katalysator durchgeleitet, um ihn vollständig vom gebundenen Sauerstoff zu befreien und den verwendeten Sauerstoff restlos in Wasser zu verwandeln. Auf diese Weise wurden drei Sorten von Wasser je aus den drei Sorten von Sauerstoff und dem leichten Wasserstoff hergestellt. Die so gewonnenen Arten von Wasser wurden alle sorgfältig gereinigt und ihre Dichte wurde je mit der des Standardwassers mittels eines Quarzschwimmers verglichen. Aus diesem Experiment ergab sich folgendes:

(1) Das Wasser, das aus dem Sauerstoff (III), d.h. dem kompletten Sauerstoff aus Wasser entstand, erwies sich durchschnittlich um 2γ schwerer als das Wasser aus dem Sauerstoff (II), der durch die partielle Elektrolyse des Wassers hergestellt wurde. Daraus folgt, dass der Trennfaktor von Sauerstoffisotopen unter den von uns verwendeten Versuchsbedingungen d.h. bei der Elektrolyse von 2N NaOH Lösung zwischen Nickel-Elektroden $O^{18}/O^{16} = 1.01$ ist. Dieser Wert erwies sich als gut übereinstimmend mit den von Johnston[1] sowie von Taylor und seinen Mitarbeitern[2] gefundenen.

(2) Wie erwartet erwies sich das Wasser aus dem Luftsauerstoff (I) spezifisch schwerer als das aus dem Wassersauerstoff (III) gewonnene. Der Unterschied betrug durchschnittlich 8γ. Diesen Unterschied darf man fast ausschliesslich auf den Unterschied im spezifischen Gewicht oder in der Isotopenzusammensetzung zwischen Luft- und Wassersauerstoff zurückführen. Denn unter den von uns verwendeten Versuchsbedingungen war erstens irgendeine isotopische Trennung im Sauerstoff ganz ausgeschlossen und zweitens konnte eine eventuell vorhandene minimale Trennung von Wasserstoffisotopen auf die oben geschilderten Experimentalresultate (1) und (2) keinen merklichen Einfluss ausüben. Nimmt man an, dass das Isotopenverhältnis $O^{18} : O^{16} = 1 : 500$ ist, dann folgt aus diesem Resultat, dass der Luftsauerstoff um 4% reicher an O^{18} als der Wassersauerstoff ist, oder dass der Verteilungskoeffizient von O^{18} zwischen Luft/Wassre $= 1.04$ ist. Auf die Frage nach der Ursache dieses Unterschiedes kann man natürlich nicht sofort antworten. Aber es scheint uns interessant, dass der eben gefundene Koeffizient vielmehr dem von Urey und Greiff[3] aus spektroskopischen Daten errechneten Verteilungskoeffizienten von O^{18} beim Austauschgleichgewicht zwischen Sauerstoff/Wasserdampf ($= 1.020$) nahe steht, aber nicht dem zwischen Sauerstoff/Wasser ($= 1.006$). Auf jeden Fall

(1) H.L. Johnston, *J. Am. Chem. Soc.*, **57** (1935), 484.
(2) P.W. Selwood, H.S. Taylor, J.A. Hipple, Jr., und W. Bleakney, *J. Am. Chem. Soc.*, **57** (1935), 642.
(3) H.C. Urey und L.J. Greiff, *J. Am. Chem. Soc.*, **57** (1935), 321.

muss bei genaueren Versuchen die oben gefundene Tatsache in Betracht gezogen werden, dass es einen ziemlich merklichen Unterschied in den Isotopenzusammensetzungen zwischen Sauerstoff in Luft und Wasser, den zwei wichtigsten Behältern von Sauerstoff, gibt und dass er schon auf die vierte Dezimalstelle des Atomgewichts des Sauerstoffs einen Einfluss ausübt. Die bisher manchmal beobachteten Diskrepanzen zwischen den von vielen Forschern veröffentlichten Daten über den Trennfaktor von Sauerstoffisotopen sowie das Vorkommenverhältnis von Wasserstoffisotopen scheinen uns mindestens teilweise durch die eben gefundene Tatsache befriedigend erklärt werden zu können. Näheres darüber soll später in diesem Bulletin erörtert werden.

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THE CONFIGURATION OF CHLOROBISDIMETHYL-GLYOXIMOAMMINE-COBALT.

By Ryutaro TSUCHIDA, Masahisa KOBAYASHI, and Akira NAKAMURA.

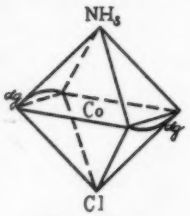
Received December 18th, 1935. Published January 28th, 1936.

The authors have recently published a paper[1] on asymmetric adsorption of quartz and proposed a convenient method for detecting molecular asymmetry. It affords the means of revealing optical activity of racemic substances even when the traditional methods for resolution are unavailable. In the present paper is given one of the conspicuous examples of this method.

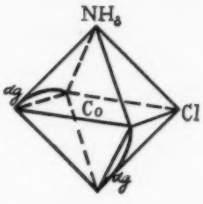
The steric configuration of chlorobisdimethylglyoximoammine-cobalt [Codg_2(NH_3)Cl] has not yet been determined. For this non-electrolytic ammine may be assumed two possible configurations, i.e., cis- and trans-forms (Fig.). If we could prove optical activity in the ammine, the configuration should consequently be of the cis-form, i.e. [Codg_2(NH_3)Cl$^{(1)}_{(2)}$]. The ammine, how-

(1) R. Tsuchida, M. Kobayashi, and A. Nakamura: *J. Chem. Soc. Japan*, **56** (1935), 1339.

ever, would not combine with active acids or bases to form resoluble diastereomers and the crystals have so far failed to give any enantiomorphic faces. In order to determine the configuration the authors applied the new metod making use of well-developed enantiomorphic crystals of quartz of various localities, Brazil, Kimbusen (Yamanashi Prefecture) and Naegi (Gifu Prefecture). The rock-crystals from Kimbusen were transparent quartz with large trapezohedral faces and the crystals from Naegi were smoky quartz with well-defined form and beautiful lustre. The latter species occurs often as twins of the Dauphiné type and it has been supposed to have irregular internal structure in spite of its well-defined external form. One of the purposes of using this species was to have some information about the internal structure of this interesting mineral. The authors, therefore, chose a left-handed single crystal and a right-handed twin of the Dauphiné type.



Trans-form
$[Co\,dg_2(NH_3)Cl^{(1)}_{(6)}]$



Cis-form
$[Co\,dg_2(NH_3)Cl^{(1)}_{(2)}]$

The ammine prepared from chloropentammine cobaltic chloride by the method of Tschugaeff[2], was dissolved in water at 50°C. and 10 c.c. of the warm saturated solution was shaken with g g. of quartz powder. When cold the supernatant solution was syphoned out for polarimetry. It rotated the plane of polarized light by α_c degrees for the C-line in a 4 cm. tube.

Locality	Crystal	g	α_c
Brazil	right-handed	1.03	−0.03
	left-handed	3.94	+0.00
Kimbusen	right-handed	2.43	−0.05
	left-handed	1.42	+0.02
Naegi	right-handed	5.55	−0.02
	left-handed	2.93	+0.03

The solution over left-handed quartz is dextrorotatory for the C-line and lævorotatory over right-handed species. The explanation of the effect is that the ammine is a racemic mixture of *d*- and *l*-isomers and the powder of quartz which has asymmetric structure in itself adsorbs molecules of one of the antipodes of the ammine more strongly than the other. In other words, the phenomenon of asymmetric adsorption takes place. The configuration of the ammine has thus been determined as $[Codg_2(NH_3)Cl^{(1)}_{(2)}]$ instead of $[Codg_2(NH_3)Cl^{(1)}_{(6)}]$.

(2) L. Tschugaeff, *Ber.*, **39** (1906), 2695.

It is noteworthy that, so far as the sign of rotation is concerned, $[Codg_2(NH_3)Cl\{^{1}_{2}\}]$ shows the same effect as similarly configurated cobalt ammines, e.g., $[Coen_2(NH_3)Cl\{^{1}_{2}\}]^{++}$, in spite of their different electrical charges. We may, therefore, assume that similar configurations give rise to similar asymmetric adsorption[3].

It is also interesting to note that the smoky quartz from Naegi shows the same specificity as other rock-crystals, though the effect produced by the right-handed twin crystal was observed a little less than that of the corresponding left-handed single crystal. It may, therefore, be concluded that the mineral species retains, at least locally, the same asymmetric structure as shown by the external form. As the left-handed quartz from Brazil had scarcely shown the effect, the experiment was repeated with greater quantities of the quartz, but the results were always negative, while the smallest quantity of the corresponding right-handed quartz was sufficiently effective. This fact may be explained by assuming that the crystal was racemic, as in the case of the twin of the Brazil law, in spite of its external asymmetric form. The utmost caution should, therefore, be paid to the choice of crystals.

The authors have tried similar experiments with quartz powder covered with monoatomic layer of nickel, as was used in the researches by Schwab, Rost and Rudolph[4] on asymmetric catalysis. The results, however, were negative.

The authors wish to express sincere thanks to Prof. Y. Shibata for his kind advice and suggestions and also to Mr. K. Masutomi for the fine crystals from Brazil and Kimbusen.

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(3) *J. Chem. Soc. Japan*, **56** (1935), 1342.
(4) *Kolloid-Z.*, **68** (1934), 157.